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NEW YORK, JULY 11, 1927

Tautomerism of Aminated Dyes with Variation in Concentration[1]

By WALTER C. HOLMES

(One Hundred and Twenty-eighth Contribution from the Color Laboratory, Bureau of Chemistry, Washington, D. C.)

A PRELIMINARY investigation of concentration effects with dye solutions[2] showed that many aminated dyes undergo radical alterations in color and absorption spectra when their concentration in aqueous solutions is varied. They exist in a state of transition between two structural forms, molecular rearrangement occurring as the concentration of the solution is varied. It was concluded, subsequently,[3] that this tautomerism is conditioned upon the interplay of residual affinity of solvent and solute. The investigation here reported was undertaken to obtain further evidence on that hypothesis.

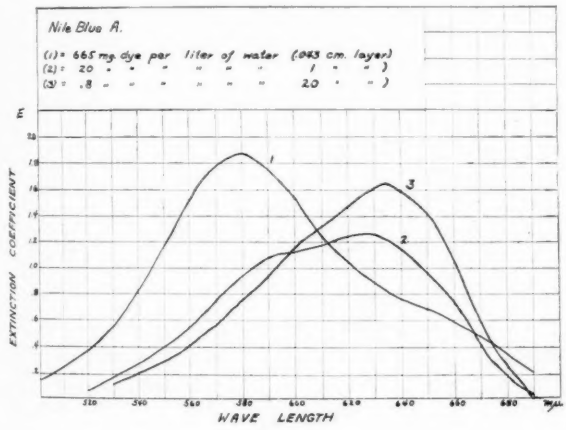

FIG. 1

EXPERIMENTAL

Three basic dyes, Crystal Violet (C. I. No. 681), Nile Blue A (C. I. No. 913) and Methylene Blue (C. I. No. 922), and an acid dye, Pontacyl Violet C4B (C. I. No. 698), were selected. The tautomerism of Crystal Violet and of Methylene Blue with change in concentration in aqueous solution was illustrated in the first paper.[2] The analogous phenomena with Nile Blue A and with Pontacyl Violet C4B are shown in Figs. 1 and 2.

Although it was known that the concentration effects in question do not originate in variation in hydrogen ion concentration, it was considered necessary to determine whether or not they are affected in any appreciable degree by that factor. Relatively concentrated aqueous solutions of the dyes were examined in a 0.043 cm. layer. The

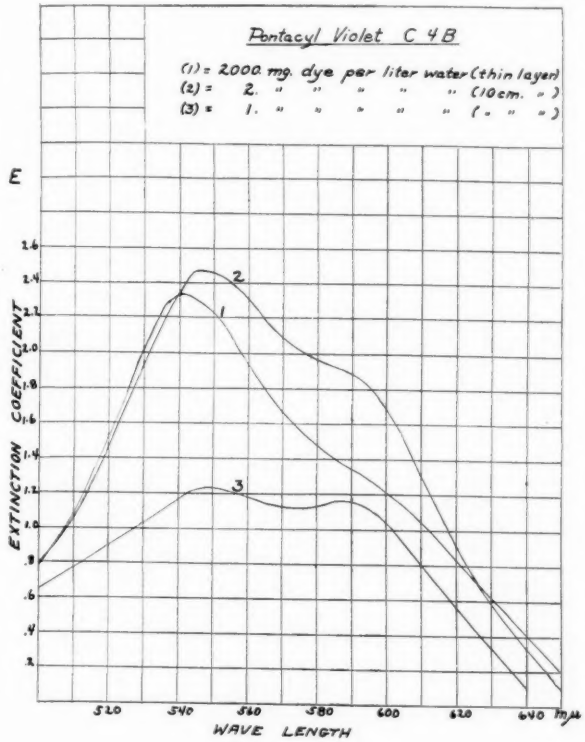

FIG. 2

[1] Received June 23, 1927.

[2] Holmes, Ind. Eng. Chem. **16,** 35 (1924).
[3] Holmes, J. Am. Chem. Soc. **46,** 2118 (1924).

standard M/20 buffer solutions of Clark[1] were employed, with the exception of his phthalate-sodium hydroxide mixtures, which form insoluble phthalates with basic dyes. Citric acid—secondary sodium phosphate mixtures —were used in obtaining pH 3, 4 and 5 buffers. In order to minimize salt effects upon the dyes, the buffer solution content of the dye solutions on which the measurements were carried out was made only 20 per cent.

The absorption of the dye solutions was determined throughout the visible spectrum. In reporting the results of the examinations, however, it is convenient to record merely the ratios of the extinction coefficients of the solutions at the approximate maxima of the "concentration forms" of the dyes to their extinction coefficients at the approximate maxima of their "dilution forms." Such ratios afford a very sensitive index of alteration in the tautomeric equilibria under investigation.

TABLE I—INFLUENCE OF HYDROGEN ION CONCENTRATION

	Methylene Blue (400 mg per l) E at 660 mu / E at 600 mu	Crystal Violet (200 mg. per l) E at 590 mu / E at 540 mu	Nile Blue A (800 mg. per l) E at 635 mu / E at 580 mu	Pont. Violet C4B (1,000 mg. per l) E at 595 mu / E at 540 mu
pH 1.....	(0.46)	....	....	....
2.....	0.52	....	0.50	....
3.....	0.51	(1.01)	0.51	0.26
4.....	0.44	0.95	0.49	0.30
5.....	0.45	0.96	0.49	0.37
6.....	0.45	0.98	0.50	0.40
7.....	0.46	1.02	0.50	0.44
8.....	0.47	1.04	0.51	0.38
9.....	0.46	(1.00)	....	....
10.....	0.47	....	....	....
11.....	0.47	....	....	....
12.....	0.47	....	....	....

With the basic dyes the only indication of a definite (although small) hydrogen ion effect is found with Crystal Violet over the range pH4 to pH8. It appears probable that this arises from colloidal alteration in the solution rather than from any actual disturbance of the tautomeric equilibrium, as it disappeared upon the strong dilution of the dye. Over the same pH range the corresponding ratios of solutions containing 10 mg. of dye per liter in 1 cm. layers remained constant at 1.50 to 1.51.

Pontacyl Violet C4B showed a more decided effect which persisted in much more dilute solutions. With this dye, however, it was noted that only the absorption at 595 mμ varied appreciably. That at 540 mμ remained nearly constant. Very similar effects have been observed with a number of dyes in the presence of neutral salts. Any actual disturbance of the tautomeric equilibrium would involve simultaneous alteration of an opposite order in both forms of the dye. When the modification of the absorption of one form of the dye is decidedly disproportionate to that of the other, as in the present instance, it appears reasonable to assume that the phenomenon results from variation in molecular aggregation, or other causes, rather than from actual tautomerism.

It appeared inadvisable to extend the ranges investigated in view of the instability of color which renders accurate measurements difficult under more alkaline conditions and the radical alterations in color which occur with salt formation at unsaturated amino groups under more acid conditions. Such further measurements as were made gave no indication of any appreciable tautomeric change. The persistence of the tautomeric equilibrium with Methylene Blue during the conversion of the dye into its di-acid salt is illustrated in Fig. 3.

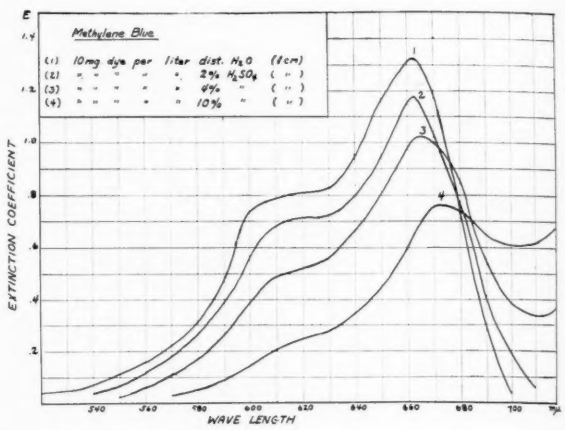

FIG. 3

So far as may be judged, hydrogen ion concentration has little or no effect upon the equilibria under investigation.

The original investigation[2] showed that alcoholic solutions of such dyes were essentially stable to variation in concentration and contained the dye in its "dilution form" only. Subsequently it has been shown that approximately the same conditions are obtained

TABLE II—INFLUENCE OF ACETIC ACID

Acetic Acid	Methylene Blue (200 mg. per l) E at 660 mu / E at 600 mu	Crystal Violet (200 mg. per l) E at 590 mu / E at 540 mu	Nile Blue A (500 mg. per l) E at 635 mu / E at 580 mu	Pont. Violet C4B (1,000 mg. per l) E at 595 mu / E at 540 mu
5%	0.97	1.28	0.70	0.34
10	1.34	1.40	0.82	0.40
15	1.71	....	....	....
20	2.03	1.60	1.22	0.63
25	2.30	....	....	....
30	2.52	1.72	1.72	1.07
40	2.78	1.79	2.34	1.54
50	2.90	1.76	2.53	1.79
80	3.04	1.77	....	....

[1] "Determination of Hydrogen Ions," 1920.

with 50 per cent of alcohol and 50 per cent of water.[5] The results given in Table II were obtained in an investigation of aqueous-acetic acid mixtures.

The results are of the same general type as those obtained with aqueous alcoholic mixtures. Nearly complete conversion into the "dilution forms" of the dyes is obtained with 50 per cent acetic acid. (The ratios employed are such that very minor variations in the dyes exert a decided effect upon the numerical values of the ratios as complete conversion into the "dilution forms" of the dyes is approached.)

With the same experimental conditions the corresponding ratios obtained with 50 per cent water and 50 per cent acetone were 2.94 for Methylene Blue, 1.71 for Crystal Violet, 2.40 for Nile Blue A and 1.71 for Pontacyl Violet C4B. The influence of acetone upon the tautomerism of the dyes is very similar to that of acetic acid.

With 25 per cent of citric acid the Nile Blue A ratio obtained was 0.92 and with 40 per cent of the acid the Methylene Blue ratio was 1.76. The hydrogen ion concentration of strong citric acid solutions is too great to admit of its employment with the two remaining dyes.

Methylene Blue gave a ratio of 1.71 with 28 per cent of urea and 2.14 with 40 per cent. Crystal Violet gave a ratio of 1.59 with 40 per cent of urea. Nile Blue A gave a ratio of 1.01 with 25 per cent of urea. An undetermined quantity of urea shifted the ratio of an aqueous solution of Pontacyl Violet C4B from 0.35 to 0.93.

The addition of acetic acid, citric acid, alcohol, acetone or urea to relatively concentrated aqueous solutions of the dyes, therefore, has the same effect upon them as does extended dilution with water, resulting in the conversion of the dyes from their "concentration forms" into their "dilution forms." Obviously the molecules of these substances effect the tautomerism. The only property which these diverse substances have in common is their unsaturation. Evidently they can influence the dye molecule only by the operation of residual affinity. On this assumption it would be anticipated that the effectiveness of a compound in bringing about the tautomeric alteration in the dyes would, in some degree, be susceptible of correlation with its degree of unsaturation. That such is the case is indicated by the following tests.

The comparative effects of 20 per cent of isopropyl alcohol and 20 per cent of allyl alcohol were measured (Fig. 4).

As would be expected, the effect of allyl alcohol is appreciably greater than that of isopropyl alcohol.

Of cyclic derivatives, m-phenylenediamine hydrochloride was tested against m-phenylenediamine (Fig. 5).

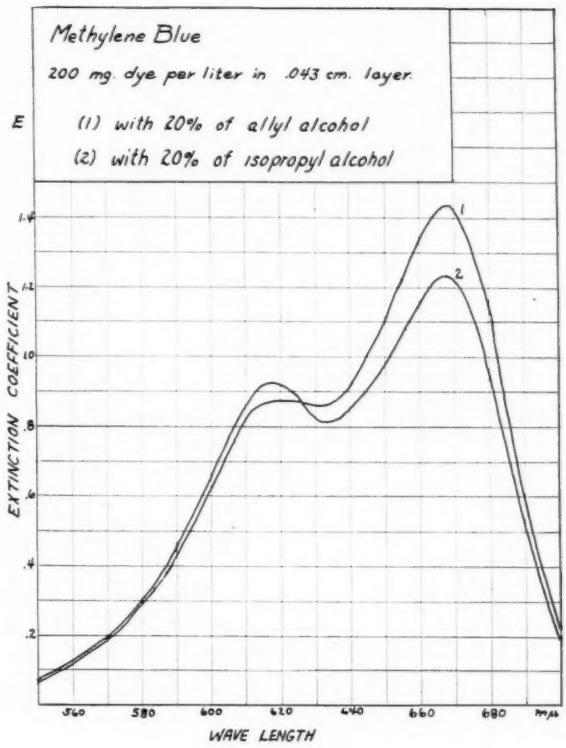
Methylene Blue
200 mg. dye per liter in .043 cm. layer.
(1) with 20% of allyl alcohol
(2) with 20% of isopropyl alcohol
E
EXTINCTION COEFFICIENT
WAVE LENGTH
560 580 600 620 640 660 680 mμ

FIG. 4

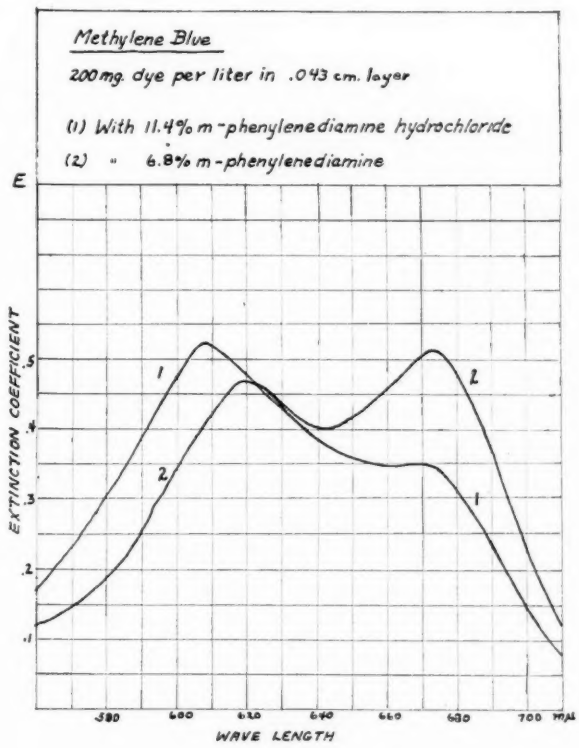
Methylene Blue
200mg. dye per liter in .043 cm. layer
(1) With 11.4% m-phenylenediamine hydrochloride
(2) " 6.8% m-phenylenediamine
E
EXTINCTION COEFFICIENT
WAVE LENGTH
580 600 620 640 660 680 700 mμ

FIG. 5

[5] Holmes, American Dyestuff Reporter, 15:247 (1926).

As would be expected, the effect of the hydrochloride is decidedly smaller than that of the base. The solution of the base employed in this test was prepared from one of the hydrochloride and contained, accordingly, a minor proportion of salt. In a further test with 8 per cent of pure m-phenylenediamine base a methylene blue ratio of approximately 2.8 was obtained. This extreme effect appears consistent with its highly unsaturated nature.

In conclusion, reference may be made to the practical application of certain of the facts brought out in the present investigation to spectrophotometric technic. It has been pointed out previously that anamalous concentration effects may be avoided in the spectrophotometric evaluation of such dyes as are under discussion by modifying the technic so that all critical measurements are made at nearly identical concentration of actual dye. Where this course is impossible, as in the analysis of dye mixtures, the use of alcohol-water mixtures containing at least 50 per cent of alcohol was recommended. Acetic acid and acetone have now been shown to be as effective as alcohol in stabilizing the absorption of such dyes to variation in concentration, and either may be employed for the purpose in place of alcohol.

SUMMARY

The tautomerism of aminated dyes with variation in dye concentration in aqueous solutions is unaffected by variations in hydrogen ion concentration. It is brought about by the residual affinity of the solvent, and the effect of the addition of unsaturated substances is equivalent to that of great dilution with water.

Alcohol, acetic acid or acetone may be employed in spectrophotometric technic in stabilizing the solutions of such dyes to variation in concentration.

Naphthol AS on Silk

A Communication from the Naphthol AS Experimental Laboratory, I. G. Farbenindustrie Aktiengesellschafft, Offenbach, a. M., Germany.

By H. LINT

Translated from Melliand's Textilberichte by Carl Toepler

IN the dyeing of natural silk at the present time, the acid and basic dyestuffs are chiefly used on account of their brightness, but these colors leave much to be desired in regard to fastness.

For a number of special fabrics the diazo colors come into use, but for fastness to light, acid, washing, boiling and bleaching the mordant and Indanthrene dyestuffs must be used.

The recent demand all over the world for increased fastness has presented a problem to the silk dyer. To a certain degree it was possible for the silk dyer to meet the requirements, but in the past few years the demand for fastness in dyeings has increased, so that the dyer is often at a loss as to which dyestuffs to use to obtain the desired shade and the required fastness.

Particularly high demands for fastness are made on those dyeings which must withstand a boiling-off with raw silk and white cotton and bleaching with hydrogen peroxide or sodium peroxide. The Indanthrene and other vat dyestuffs are the most suited type of color for this class of work.

With these dyestuffs, however, deep and bright dyeings in all shades cannot be obtained. Besides this, deep shades are comparatively costly.

The numerous demands of the trade have forced the dyestuff manufacturers to seek products and processes by means of which faster dyeings on silk can be obtained. The Naphthol AS products of the I. G. Farbenindustrie Aktiengesellschaft, which have been introduced in the cotton and artificial silk dyehouse to a large degree, can also be used for silk, and in many cases will supply the requirements for fastness now demanded.

At the present time there are ten naphthols and twenty bases of the Naphthol AS series on the market with which can be obtained various yellow, orange, pink, scarlet, red, Bordeaux, garnet, brown, blue and black shades on cotton and other vegetable fibers, as well as on artificial silk.

The usual methods of dyeing, however, are not suitable for the dyeing of natural silk, and it required many experiments to remove all the difficulties which arose.

At the present time these difficulties have, for the greater part, been removed, and the process is no longer limited to the experimental stage, but is applicable to the practical dyeing of natural silk.

Japanese silk manufacturers have been particularly interested in the process and have applied it to the manufacture of silk pieces dyed with Naphthol AS and Indanthrene colors.

The dyeing process, as with cotton and artificial silk, depends upon two operations:

(a) The preparing of the silk with a solution of the naphthol.

(b) The developing of the prepared silk in a solution of the diazotized base.

The naphthols are dissolved by the addition of caustic soda and can only be kept in strongly alkaline solutions

to which some Turkey Red oil or other substance of similar properties has been added. The Turkey Red oil must be free from ammonia.

Silk is well known to be very sensitive to the action of alkalis. The feel, luster and strength are very easily impaired if care is not exercised in handling.

It was therefore necessary to find a substance which would prevent the damaging influence of the caustic alkali. The well-known fiber-protecting agent for animal fibers, Protectol, which has found considerable use in wool scouring and dyeing can also be used here to great advantage.

It was found that the Protectol not only protects the silk against the damaging effects of the caustic alkalis, but also causes a uniform absorption of the naphthols to take place.

Comparative experiments have shown that Protectol I Double Powder is the most suitable as an addition to the preparing bath.

In order not to damage the luster or feel of the silk, the amount of Turkey Red oil in the prepare bath must not be more than 2 to 3 c.c. per liter. Naturally, the amount of caustic soda for dissolving the naphthols must be kept to a minimum.

Due to the reduced amount of Turkey Red oil, a small addition of freshly dissolved animal glue (which must not be more than one day old), besides the Protectol, has the property of causing the naphthol solutions to remain clear.

An addition of formaldehyde is made to the diluted naphthol solution. This addition helps the wet material to withstand the action of the air and at the same time increases the stability of the naphthol solution. An exception to this is with Naphthol AS-G and Naphthol AS-BR. Solutions of these naphthols should contain no formaldehyde, as their dyeing properties are nearly destroyed thereby.

The formation of the naphthol-formaldehyde compounds takes place if the formaldehyde is added to the naphthol solution at high temperatures.

Freshly prepared naphthol solutions, upon strong dilution, have the property of separating out, due to their tendency to hydrolyze.

The silk prepared in the naphthol solutions possesses a greenish-yellow color, depending somewhat on the particular naphthol used.

The development of the naphtholated yarn takes place in the solution of a diazotized base. It is possible, using material prepared with a naphthol, to obtain a series of varying shades, depending upon the base used; and, conversely, the same base will produce a series of different shades with different naphthols.

If cotton or artificial silk is introduced into a solution of a diazotized base, nothing takes place—the fibers remain undyed. On the other hand, if a skein of silk is immersed in such a solution of a diazotized base, the silk becomes dyed in yellow to brown shades, depending upon the nature of the diazo solution. These dyeings can be explained by the fact that the silk forms a dyestuff with the diazo solution, acting in a certain degree as an azo component.

Incidentally, it might be mentioned that the yellow, orange and brown shades resulting by these couplings are very fast and are similar to the yellow obtained on silk with Nitrosamine, which even to-day finds considerable application.

The intensity of the dyeings with the diazo solutions varies with the bases used. Fast Red KB, Fast Red TR and Fast Scarlet TR bases dye the fiber the least.

The dyestuffs formed by the coupling of the silk with diazo compounds also occur when naphthol impregnated silk is brought into the developing baths, and the shades change strongly toward yellow to brown.

This action on the dyed shade is so great that, for example, the combination of Naphthol AS-BO and Fast Blue B Base, which ordinarily should produce a deep blue, gives a deep brownish black, while the red shades have an undesirable strong yellow cast.

In experimenting to prevent the coupling of the silk as much as possible, it was found that the silk was considerably less dyed by the diazo solutions if the developing baths were kept more strongly acid than is necessary; for example, in the dyeing of articial silk by the same methods.

After a large number of experiments were made, it was possible to determine exactly the most suitable quantity of acid (acetic or formic acids) for the various bases.

The preparation of the developing baths takes place in the same manner as the recipes given for cotton in the Naphthol AS Instruction Booklet No. 1014 of the I. G. Farbenindustrie Aktiengesellschaft. The addition of aluminum sulphate must be withheld. The formation of aluminum hydroxide and aluminum soap, which diminish the luster of the silk, occurs from the action of the aluminum sulphate and the caustic soda and Turkey Red oil of the prepare.

The diazo solution is neutralized with sodium acetate and in some cases with sodium formate.

There are three methods in use for the dyeing of Naphthol AS colors on silk:

1. The dyeing of degummed silk.
2. The simultaneous preparing and degumming of raw silk and the subsequent development.
3. The dyeing of weighted silk.

These processes differ only in the composition and application of the prepare baths. The preparation and application of the developing baths is the same in all three processes.

For European practice, the dyeing of degummed, unweighted silk should come into consideration first of all. The method of application is as follows:

(a) *Preparing.*—The prepare bath is made up of cold soft water and the naphthol solution, and then brought to the proper concentration with water. The extracted silk is entered in the warm (20 to 25 deg. Cent.) bath (1:30), worked for fifteen to twenty minutes, and in the

case of deep shades the silk is raised, an addition of 10 grams of common salt per liter is made, the bath well stirred, the silk again worked fifteen to twenty minutes, and, without rinsing, the material is well extracted. To prevent streaky dyeings it is advisable to wrap the silk in naphthol-impregnated cloths when extracting.

(b) *Development.*—The well-extracted silk is entered in the cold dye bath (maximum temperature 20 deg. Cent.) containing the proper amount of neutralized diazo solution and 10 grams common salt per liter, turned several times and dyed for one-half hour.

After developing, the silk is freed from the diazo solution through repeated rinsing in cold water.

The material is then soured in a warm bath of hydrochloric acid, rinsed, followed by a warm soda bath (2 to 3 grams soda ash and 1 to 1½ grams Protectol II Double Powder per liter), and again rinsed warm. It is then soaped twice below the boil in a bath containing 4 to 5 grams Marseilles soap per liter, rinsed warm and cold, and finally brightened in a bath of acetic, formic or sulphuric acids.

For the simultaneous degumming and dyeing of raw silk, the well-known caustic soda-Protectol degumming process is combined with the Naphthol AS dyeing process. The quantity of caustic soda for the prepare bath must be increased in this process. The amount of Turkey Red oil is measured so that 1 liter of prepare bath contains not more than 2 to 3 c.c. of Turkey Red oil.

Under no conditions must formaldehyde be added, since the bath, which is worked at high temperatures, would be injured and prevent the removal of the gum present in the silk.

For the production of uniform dyeings it is quite necessary to extract or squeeze out immediately after preparing and to develop at once.

The prepare bath should contain 16 c.c. NaOH 34 deg. Be., 2 grams Protectol I Double Powder and 2 grams glue per liter.

The raw silk is entered in the prepare bath, heated to 60 deg. Cent., turned not more than three times in twenty minutes, the material raised and the bath cooled by the addition of an equal volume of cold salt solution (20 grams salt per liter; in the case of Naphthol AS-SW and Naphthol AS-BR use 10 grams salt per liter) at 20 to 30 deg. Cent, so that the ratio of silk to liquor is 1:60. The silk is again entered and worked for twenty minutes, and is then extracted at once without rinsing. The developing takes place as described under degummed silk.

Tin weighted silk is dyed in the same manner as degummed, unweighted silk. Due to the greater affinity of the naphthols for weighted silk, the quantity of naphthol is kept somewhat lower than for unweighted silk. An addition of 10 to 15 c.c. waterglass solution 25 deg. Be. per liter of prepare bath is made in order to prevent damage to the weighting and to keep the prepare bath clear.

The method of working is similar to that for unweighted silk.

It should also be mentioned that it is not desirable to work with standing baths.

The prepare baths for unweighted and weighted silks are nearly completely exhausted by the addition of salt.

For each batch of material it is necessary to add fresh prepare and developing solutions.

The majority of the Naphthol AS colors possess excellent light fastness. In many cases the fastness to light of the Naphthol AS combinations on silk are superior to those on cotton.

Moreover, the dyeings are very fast to wearing, weather, washing, water and cross-dyeing. Certain Naphthol AS combinations are fast to boiling and bleaching; that is, they withstand the degumming and bleaching processes when woven with raw silk.

Dyes and Their Application: Recent Technical Progress

Theories of Dyeing—Degree of Dispersion—Chemical Theory—Optically Active Dyes—Dyeing of Inorganic Substances

By L. J. Hooley

THE development of the technique of dyeing has been empirical rather than scientific. Even at the present time there is no generally accepted theory of the mechanism of the dyeing process, although considerable investigation has been carried out.

Investigations appear to have been carried out from entirely different angles. It might appear that different workers held entirely opposed and mutually exclusive views, and that it was still a case of deciding whether the process was a chemical one or was, say, merely physical. The solution of the problem, however, cannot any longer be considered as depending on a choice between mechanical, colloidal and adsorption ones.

The best attitude towards the problem is probably to view the whole dyeing process from as general a standpoint as possible, and to keep in mind various factors which may be of importance. Among such factors there are the condition of the dyestuff in the bath, its degree of dispersion or ionization; the properties and condition of the fiber itself and the possibilities of electric charges on its surface; the manner in which the dyestuff comes into contact with the fiber, and the succeeding stages of penetration, adsorption, solution, coagulation, precipitation of colloidal particles, or formation of compounds.

In individual cases, one or other of the above factors may assume sufficient importance to be virtually the cause of dyeing in that particular case, and to be specially favorable towards one or other of the theories. This viewpoint provides a frame of reference by means of which the significance of the various developments can be estimated.

Various aspects of dyeing theory are attracting considerable interest at the present time, and some very interesting papers have appeared recently.

On the question of giving one theory preference over another it will often be difficult to separate phenomena and label some chemical and others physical or electrical, and probably the electrical theory has the advantage of being the most general and most readily including the others.

Dyeing theory is receiving considerable attention at the present time, and as the dyer becomes more and more a chemist it will be likely to receive more.

Degree of Dispersion of Dyestuffs

The majority of dyestuffs do not, of course, form true solutions, but are in a condition between solution and colloid. Auerbach (Textilber., 1927, 160) draws very interesting parallels between the degree of dispersion and other properties. He deals principally with the substantive, acid and basic colors, and the most interesting feature is perhaps the clearly marked differences which these classes show. Speaking generally, the three classes are present in the dye bath in different conditions, and their difference in dyeing properties may be more a result of the differences between their degrees of dispersion than between their chemical constitutions, although, of course, their chemical constitution may be the deciding factor in determining the degree of dispersion in solution. The author draws a series of graphs to illustrate the distribution of dyestuffs with regard to the various degrees of dispersion. First, taking the three classes together and plotting against the degree of dispersion the number of dyestuffs having this particular dispersion, it is seen that few dyestuffs are so finely divided as to be in a state of molecular dispersion and few properly colloidal, the great majority coming midway between.

In the second diagram the author does the same thing, but considers the basic colors separately. The two curves for the basic colors and for the acid and direct colors combined, show that approximately the positive basic colors have a much higher dispersion than the negative acid and direct colors. Only a few basic colors are sufficiently aggregated to show particles as large as those of the direct colors, and it may be because they are too small that they will not dye cotton without a mordant. The substantive colors have a much lower degree of dispersion than the acid ones. In the fourth diagram the hot dye substantive colors are compared with the cold dyeing. The hot dyeing colors approach the colloidal condition, and at ordinary temperatures the particles would appear to be too large for absorption. The effect of a higher temperature is to cause disaggregation, giving a more suitable degree of dispersion for cotton dyeing.

Chemical Theory

It is in the case of the animal fibers where amino and carboxylic acid groups are known to be present that the argument for a chemical theory of dyeing is strongest, and if it is true that acid and basic colors dye wool by forming loose compounds with these amino and carboxylic acid groups, it should be possible to form compounds with simpler analogues of the amino acids present in wool and silk. Pfeiffer and Angern (Z. angew C., 1926, 253) have accordingly carried out experiments with phenylalanine and sarcosine. Phenylalanine and para-hydroxy-azobenzene were found to combine in equal proportions, as did also sarcosine and para-hydroxy-azobenzene. Sarcosine and 2:4-hydroxy-azobenzene combined in the proportions of 2-1. These products all had definite melting points and were readily dissociated in solution.

The view that dyeing wool with acid dyes consists of salt formation between the wool acting as base and the dye as acid is confirmed by K. H. Meyer and Fikentscher (Textilber., 1926, 605). By observing the adsorption of Orange I and para-sulphobenzeneazoacetanilide in both coarse and fine wool fibers, it was found that the total absorption was independent of the surface area of the wool. It was also shown that wool will combine in constant proportions with different acids. Experiments with about twenty acids of different types showed that in each case the wool combined with the same number of equivalents of the acid.

Optically Active Dyes

Since wool and silk contain optically active compounds, it is probable that if the dyestuff combines chemically with these, that enantiomorphic forms of the same dye would show different dyeing properties.

Brode and Adams (J. Amer. C. S., 1926, 2193) have prepared optically active colors by coupling diazotized d-, l- and dl-phenyl (*p*-aminobenzoylamino) acetic acid with beta-naphthol and dimethyl aniline. They were, however, unable to detect any difference in the absorption of the two active forms in dyeing experiments, or in fastness to light or other physical properties. Racemic forms, however, appear to be taken up to a greater extent than d- or l- forms. In previous work on this subject, Porter and Ihrig had claimed to have observed differences, using other active components. Brode and Adams have therefore also repeated this work, but have been unable to confirm it.

Dyeing of Inorganic Substances

Evidence in favor of the adsorption and electrical theories of dyeing have been afforded by experiments carried out on the coloring of substances such as china clay and inorganic salts. The dyeing of these substances has been found to be very closely analogous in several ways to the dyeing of fibers. Of particular interest are the effects of impurities, and of the degree of hydration of the solid substance. It is shown, for instance, by Morley and Wood (J. S. D. C., 1923, 100), that if titanic acid is prepared by separation from a solution which is slightly acid, it readily absorbs acid dyes and has little affinity for basic. Precipitation from alkaline solutions

shows opposite results, and the product from neutral solutions shows little dyeing power with either.

In the case of precipitation from acid solution the excess of positive ions may be assumed to lead to deposition of some of these on the inorganic substance. When later this substance is placed in an acid dye bath the positive ions already present on the substance will attract the colored negative ions of the dyestuff. Further recent work by Wood and Burns appears in J. S. D. C., 1926, page 187, where the behavior of hydrated chromic oxide prepared under the different conditions is examined, and in the same journal, page 211, where experiments are carried out on the absorption of Methylene Blue by zinc oxide.—The Chemical Age.

The Fiber the True Textile Unit

Common Mill Practice Considers a Swatch or a Skein as the Unit for Experimental Purposes—By Substituting the Single Fiber Many Variables Are Eliminated.

By H. A. GOODMAN

MOST textile chemists or investigators, including those who run mill experiments, use the piece of cloth or a swatch as a unit, while those in the yarn end think of a skein, a cone or a ball or beam of warp as their unit. These are convenient units for experiments, but they are far from being the true textile units. The real unit is the individual fiber or filament.

The ordinary laboratory or mill experimenter has a definite objective in desiring to obtain a particular finish or shade on a particular kind of goods. The fundamental research worker has also a definite object, but it is much more difficult. It is to obtain something approaching absolute standards and definitions of properties for textiles, and it must almost necessarily be based on the unit of which they are made —the fiber or filament.

In the commercial skein of rayon where the twist in the thread is small, the properties of the yarn and the filament are almost the same. This is the simplest case of all, for the filaments are not stuck together, but run continuously through the whole strand. The properties of the yarn are therefore those of the single filament multiplied by twenty-four, sixty, or whatever may be the number of filaments in it.

Real silk is the next to the simplest, for its single filaments run virtually continuously through the yarn. The properties of the raw silk are practically those of the cocoon filament, with the additional size and strength. In the thrown silk they are still much the same as in the raw, only the strands are larger, and are somewhat modified by the gum and twist. After the boil-off we are back to the single filament, and there is nothing very distinctive about the yarn properties in comparison with those of the single boiled-off filaments.

It is not difficult to see in these cases that the study of the filament is almost the same as the study of the yarn made from it. Owing to this relationship we have here almost the only case where fibers are inspected by actual scientific tests before making up into textiles. This is the routine raw silk testing. It does not go quite back to actual tests on the single cocoon filaments, but it covers their properties in a manner that proves satisfactory in silk manufacturing practice. Physical testing of rayon is also conducted in much the same way.

When we come to cotton and wool, or, in fact, any other yarn or fabric that is an aggregate of short fibers, their properties begin to have a different significance. One of the first and most important is the character of the fiber surfaces, and their adaptability to hold together by friction in the yarn. Some of the other properties are also directly reflected in those of the yarn. Flax fibers are inelastic and flax yarns are usually inelastic, partly because the fibers are long and lie close and flat together, usually without being highly twisted. Cotton lies more loosely in the yarn, and when it is stretched the yarn draws together or becomes consolidated. In yarn of high twist, the twist angle changes with tension, and the yarn elongates more for this reason.

Mercerized yarn or cloth, as exemplified in mercerized cotton airplane-wing fabrics, has been stretched and set in a new position. Starting at that point there is, of course, not the normal amount of stretch when a force is applied. This is not so much a function of change in fiber properties as it is of change of fiber arrangement. A linen fabric has less natural stretch than cotton, but mercerizing with high tension produces a fabric with some of the linen character. The chemical or physical change in the fibers from mercerization has something to do with the result, but evidently not so much as the new elastic or rather inelastic properties imposed on the structure of the fabric through the straightening of fibers, and perhaps some slip, which become fixed in drying.

Dyeing of cotton is strictly a fiber phenomenon, and poor dyeing from tight twists or weaves or similar causes, while it may be attributed to the yarn or

fabric, is really caused by the packing of the fiber too tightly.

Except on the single score of convenience in handling, dyeing studies really ought to be made on loose, we won't say raw, cotton. Yarn or piece goods will do for comparative tests, but it is rare that pieces of different weave, or yarns of different count or twist, will dye to equal shades in the same dye bath. The mechanical factors affect the result and prevent getting absolute values, even if it were otherwise possible. Using the loose fibers will do away with the effects of fiber arrangement, for after dyeing they can be made into some standard type of pad for color comparisons. Working along such lines one can approach nearest to a determination of the dyeing properties of cotton substance. There will still be plenty of variables, after that due to the form of the sample has been eliminated.

The question of variation between individual fibers can be settled by observing the dyed colors of separate fibers or groups that are alike. If appreciable differences are found, their effects can be overcome by suitable mixing of the loose cotton before dyeing if it is necessary or desirable to compare average results.

In wool the case is even worse. Few yarns or fabrics will dye alike in a given dye bath, but it may be the effect of actual differences in the wool even more than optical effects due to the mechanical structure of the samples. In spite of the fact that a variety of colors can be found in an ordinary lot of loose wool being dyed a compound shade, well mixed loose wool which is as uniform as possible at the start should be tried if it is desired to obtain anything approaching absolute results. Wool is probably the most difficult case, for it varies so much that anything absolute is almost impossible. However, it can only be approached through detailed definition of the fiber properties, and preferably, if it does not prove utterly impractical, through dyeing the wool loose.

The finishing of any fabric depends on the rigidity, elasticity, swelling and similar properties of the fiber substance, and in some cases on the equivalent properties of such external materials as may be combined with it. The proper conditions to obtain finishes have been learned empirically. Such are the moisture content, temperature of calendar rolls, combinations of starches, kinds of softener, time and temperature of steaming, and many others too numerous to mention, success being due to the finding of the proper combination and to sticking to it in every detail time after time.

If one would learn the fundamental principles of finishing, the proper course, and it is being followed in some of the research institutes, is to learn the properties of the fiber substance as a chemical material, or of the separate fibers as physical units so that true explanations can be worked out.

A common case in point is felting. The fulling of wool, it is true, depends on the structure of the yarn and of the piece of cloth, but more fundamentally and in some way that is not yet entirely clear, it depends upon the wool fiber and evidently upon its surface structure of characteristic scale form.

The process is more subtle than the simple interlocking of scales, so long held as an explanation, and may involve swelling and softening of the fiber substance as well as mechanical action. Whatever the explanation, felting is a fiber phenomenon.

In the processes of carding, spinning and the like, the case will be clearer because these so obviously depend on fiber length, diameter and the elastic properties. It is, however, no less true that all chemical, as well as physical processes, depend on the individual fiber, and this point of view is reflected in many of the latest papers on textile research.

The Indigosol Colors

The Printing Processes—Reason for Acid Treatment of Goods—Action of the Reserve Agents—Fast Colors on Cotton Warps—Properties of Various Indigosols

Translated by Ismar Ginsberg, B.Sc., Chem. Eng.

(Der Textilchemiker und Colorist, 1926, 117-120)

THE indigosols are the sulphuric acid esters of the leuco compounds of vat colors of any type, not only of the indigoid group but also of the anthraquinone and alizarin indigo groups. These dyestuffs are soluble in water and soda solution, and therefore their use is entirely different from that of the common vat dyes. A characteristic property of the indigosols is their relative stability towards atmospheric oxidation, but the vat color is regenerated from them by oxidation with a acid solution. This group of colors has a particular interest for the wool dyer and the calico printer, although certain members of the series are also suitable for dyeing cotton yarns and cotton and silk piece goods under certain definite conditions.

In printing fabrics with the indigosol colors it is possible to use two principal processes. One of these is the wet or nitrite process and the other the dry or steaming process.

According to the nitrite process indigosol is made up into a color paste with sodium nitrite and suitable thick-

ener, and then printed on the goods, which are then dried. Thereafter the color is developed by treatment of the printed fabric in a bath which contains 30 parts of 66 deg. Be. sulphuric acid per 1,000 parts of water, the temperature being 20 to 30 deg. Cent. and the treatment lasting fifteen seconds.

Smearing Prevented by Acid Treatment

Practical experience has shown that the acid treatment of the goods has a very important bearing on the quality of the printing. When the process was first used on a large scale, it was found that when a large open soaping machine was employed for this purpose and the printed goods were passed through a dilute sulphuric acid contained in this machine, the first portion of the goods treated were smeared with Indigo. This was found to be due to the fact that Indigosol O is so easily soluble that a certain portion was washed out of the goods into the acid liquor before oxidation took place.

Not only was color lost but the white portions of the printed fabric were dyed with the Indigo. It was found that this could be prevented by slop-padding the printed fabrics with the acid solution. An apparatus suitable for this purpose consists of a low, wooden vat which contains the acid and in which there is placed a wide wooden roller covered with felt. Thus the fabric will not come into direct contact with the acid, but will pass over the roller. Surface contact only takes place, the impregnation period is of brief duration, and thus the time required for the full development of the color is attained by allowing the fabric to pass through the air for a short distance before it enters the first wash tank. This process is very similar to the one employed in the development of Para Red.

A mild degree of oxidation is produced by the nitrite process, on the assumption that the acid is not too concentrated and a considerable excess of nitrite is not employed.

The strength of the sulphuric acid solution must be between 2 and 4 deg. Be., and the temperature must be maintained at the point which is optimum for each individual indigosol. For example, Indigosol O can be oxidized with comparative ease and hence it is easily over-oxidized; hence the temperature of the acid solution is prevented from rising above 38 deg. Cent. On the other hand, the ester salt of tetrabromoindigo, which is Indigosol 04B, will not be properly developed under a temperature of 60 deg. Cent.

Indigosol O gives very fine Indigo shades on certain calicoes, particularly in the development of a single Indigo Blue shade, whether directly or by the reserve printing process on the wet fabric. This process can also be used with good results for the production of reserve effects with vat dyestuffs. The latter are printed in the customary manner with alkali and hydrosulphite, and the nitrosoamines of different insoluble azo colors are used for the printing of Indigo Blue, for the reason that steaming is not necessary.

However, there always exists the possibility that the naphthol preparation will be oxidized in the unprinted portions of the fabric, and when this happens it is not any easy matter to remove the defect. This trouble can, nevertheless, be avoided if the quantity of nitrite is reduced to a minimum and a small proportion of a reducing agent is added to the sulphuric acid solution. Many colors may be used in addition to the Indigosol, but before this can be done a change in the method of using the sulphuric acid bath must be worked out.

The dry process is similar to the one customarily employed in Aniline Black practice. The oxidation of the indigosol is effected with the aid of sodium chloride in the presence of a small amount of vanadium salt, used as a catalyzer. The required acidity of the bath is obtained through the use of a salt which remains neutral up to the steaming point. Various ammonium compounds are well suited for this purpose, and of these ammonium sulphocyanide is the most suitable. This salt is very stable in the cold, but it is immediately decomposed during the steaming and yields sulphocyanic acid.

Action of Reserve Agents on Indigosols

One of the many advantages of the indigosols consists in the ease with which they are acted upon by reserve agents, without their being any danger of injuring the cotton. An alkali or a reducing agent prevents the regeneration of the vat dye from the indigosol, the former preventing the formation of acid and the latter the oxidation. Sodium acetate and sodium thiosulphate exert the most powerful reserve action, as when they are used any dyestuff can be employed which will fix itself on the fibers. Indigosols are not printed with discharge agents after their full development, but they are treated with a reserve agent before the discharge media are employed.

In order to obtain reserve effects, the material is printed in the white condition and then slop-padded with the indigosol solution, or it may first be slop-padded with the indigosol solution and then printed with the reserve dye, before the color is developed. The former process is preferred.

The vat colors can be used as reserves with the different indigosols without any change in the process, as in the ordinary vat bath there are always present sufficient amounts of reducing agents and alkalies to hold back the development of the ground color. Experience has, nevertheless, shown that there is a certain difficulty in the use of the ordinary vat colors for this purpose. In printing certain designs a definite minimum of alkali and hydrosulphite must be present to obtain proper fixing of the vat color. However, when ground color slop-padded over, the vat dyestuff is pale, then the minimum proportion of hydrosulphite and alkali, as mentioned above, is more than sufficient to produce the correct reserve effects on the ground. A dyestuff which depends on the

use of the correct reserve medium for obtaining suitable fixing of the color on the textile fiber can scarcely be considered as the ideal reserve.

Another difficulty with the use of the vat dyestuffs appears during the steaming of the material which has been printed in deep colors. It is undoubtedly true that the production of the ground color depends on the oxidation process, while the fixing of the vat dyestuff depends on a reducing action. For this reason the temperature in the steaming apparatus must be maintained at a very carefully regulated point at the beginning of the operation. Maintenance of the temperature at this constant point for a prolonged length of time is of a difficult matter, but when it is not done the printed goods will be faulty.

All these difficulties can be avoided when use is made of the nitrite process in obtaining reserve effects with certain desirable vat dyestuffs. In accordance with this process the material is first slop-padded, then dried, printed with the reserve paste, dried again, steamed in the Mather-Platt apparatus with moist steam at a temperature of 110 deg. Cent. and thereafter the ground color can be developed in the manner described above, by slop-padding with the aid of sulphuric acid. It is particularly worthy of mention that the treatment with sulphuric acid has a very favorable effect on the oxidation of the vat dyestuff in that much clearer and fuller tones are obtained than is customary in the well-known vat dyestuff-discharge printing process on a tannon mordant and with subsequent dyeing with basic colors.

The interesting and furthermore most suitable dyestuffs for the production of colored resists on an indigosol ground are the so-called chrome colors. They are of special interest due to their fastness towards soaping at a boiling temperature, even in the case of those which are not affected by other methods of treatment, being materially enhanced when they are employed as reserves on indigosol grounds. This valuable property makes the chrome dyestuffs particularly well suited for the manufacture of Foulard articles in common with the indigosols.

Fast Colors on Cotton Warp

The indigosol dyestuffs are also well suited for the printing of fabrics by hand and for printing yarns, for, the printing paste, as well as the printed materials, are fast, especially when the nitrite process is employed. Cotton can be slop-padded with indigosol dyestuffs by the nitrite process, the cotton being in the warp condition, and then it can be woven in the cloth with cotton filling in the raw condition. The resulting fabric will remain in this condition particularly over an indefinite period without the color being developed. This observation suggests the possibility that the indigosols can be used for obtaining fast printed colors on the cotton warp in cretons. This has not been possible heretofore when vat dyes are employed.

The most important of the indigosol marks are as follows:

Indigosol O, 1924.—A stable Indigo compound soluble in water and suited for the production of Indigo Blue shades according to the processes mentioned and also for the dyeing of woolens.

Indigosol O4B, 1924.—This is also a stable Indigo compound, soluble in water, and is used for the production of bright blue shades. It is particularly well suited for calico printing and especially for direct printing. In contradistinction with Indigosol O, Indigosol O4B is more easily developed with chlorates after steaming, than by the nitrite process without steaming. Its fastness properties are comparable to those of Brilliant Indigo 4B and the like.

Indigosol Yellow HCG, 1925.—A stable color, soluble in water and used for obtaining old gold shades on cotton as well as in direct printing. It is developed at best by the steaming process, and can also be used on wool and silk.

Indigosol OR, 1925.—A stable color, soluble in water, yielding marine blue tones. Mostly used in calico printing, and is suited for reserve printing as well. Its fastness corresponds to that of Indigo MLB/R. The color is developed by the nitrite process, as well as by steaming. Bright blues are obtained.

Indigosol Violet AZB, 1925.—Has all the characteristic properties of the indigosols, and yields violet shades which are fast to light, washing and chlorine. It is recommended for the printing of fabric, both by the direct and the resist processes. It has been found that the best results will be obtained when the color is developed by the steaming process.

Indigosol Black TB, 1926.—Yields black and grayish shades. This dyestuff is also well suited for the printing of fabrics, both by the direct and resist methods. The resistance of the printed shades is satisfactory as far as washing and chlorine are concerned.

Indigosol Rose HR Extra, 1926.—Is another member of this series which gives shades that are particularly fast to washing, to chlorine and to light. These shades are of a brilliant rose color. The dyestuff is recommended for use in the printing of calico, and the color is best developed by steaming.

Indigosol Orange HR, 1926.—Is a new member of the series which gives brilliant orange shades, and is principally suited for the printing of calico. It is also recommended for resist printing. Its fastness to washing and to chlorine is very satisfactory, and its fastness to light is good. This dyestuff is also best developed by the steaming process.

Indigosol AZG, 1926.—Is one of the most recent additions to this group of dyestuffs. Its properties are very similar to those of the rest of the series which have been described above. Furthermore, it is employed in the same manner. It yields very useful greenish blue shades.

Indigosol Red HR, 1926, which is also a new product, yields bluish red and rose shades. Just like the rest of the members of this series it is very well suited for printing of calico. The shade, developed by steaming, is particularly fast to washing, chlorine and light.

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SAID THE LAUNDRY MAN—

THE Curious Visitor from New England set out one day to inspect the Modern Laundry, which was located in the suburbs of a small textile city. The building which housed the laundry was new, and with its many windows and well-kept front lawn reminded the Visitor of those model bakeries he had seen pictured in bread advertisements. He entered and was ushered to the outer office of the proprietor. While waiting he glanced through the pages of a magazine which lay on the table.

When the laundry owner entered the Curious Visitor introduced himself. "I own a textile mill," he said. "I have often desired to follow the course taken by my goods after they have been converted into apparel, and so I am devoting a week of my vacation this year to the study of the consumer and apparel trades. My travels have led me here, where I hope to see the processes through which goods must pass to be laundered."

"Fine," said the laundry owner. "I see that you have been sufficiently interested in our business to read something about it," and he indicated the trade journal which the Visitor had found on the table.

"I have been reading about the technical research that your industry is undertaking," said the Visitor. "I learned something new. Such research is a good thing, no doubt. You laundry men seem to have started in the right direction."

"Yes," agreed the laundry owner, "our studies at Mellon Institute, University of Pittsburgh, are following very practical lines, and so far have yielded some interesting results. The members of our trade have learned many helpful things about the chemical processes of laundering. Our research has taken us into your business—textile manufacturing. Our chemists at Mellon are determining why some fabrics cannot be laundered, why some garments fade and shrink even under standard laundry practice, and why the laundries should not always be held liable for damaged goods. Our study of textile processing has led to experiments with dyes and fabrics of every kind; some of the results have shown us where to change our laundry practice to improve the quality of our work and avoid trouble over claims. But we have also learned that too frequently fabrics are defective before they reach our wash-wheels because they have not been made properly; some process in their manufacture—the bleaching or dyeing or finishing, perhaps—has rendered them unfit to stand ordinary laundering."

"That does not look so well for us," put in the Visitor meekly. "Cannot the manufacturers prove that their processes are right?"

"You have compiled very little technical data to support any proof. Presently I shall tell you why," replied the laundry man. "But in this matter of research we are not the only branch of the consuming trades, as you call them, to recognize the need of improving our technical processes. Our colleagues, the cleaners and dyers, have also been awake to the situation in the textile industry. I have kept informed on what they are doing because the Laundryowners' National Association, of which I am a member, is co-operating with the National Association of Dyers and Cleaners. The latter group has a research associate and several assistants working at the Bureau of Standards in Washington, studying dry cleaning as related to the construction and processing of fabrics. They also have accomplished some splendid chemical research, such as an investigation on the effects of dry cleaning on weighted silk. Their work is planned systematically. This year's program of research includes three important studies: one on the subject of soaps and detergents, another on the discoloration of fabrics due to corrosion from metal, and a third investigation into dyestuffs on fabrics with a view to cataloguing those affected by cleaning solvents.

"These dyers and cleaners have stirred up a lively interest in their activities among allied trades. A conference held last year in New York by their association was attended by representatives of thirty branches of the apparel trades and others interested in textile research. They are trying to keep inferior goods out of the market and prevent at the outlet many damage claims wrongly laid at the cleaner's door.

"Furthermore, the dyers and cleaners are erecting at Washington a research building in which their laboratory studies will be carried on under ideal conditions. All this has been financed by the members of the trade, co-operating through their national association. In this way $125,000 was subscribed for the building of the new institute."

"Remarkable," assented the Curious Visitor, "and admirable co-operation. Since you are so well in-

formed on textile research, perhaps you can tell me something about what is being done in my branch of the industry. Being concerned wholly with the commercial aspects of my business, I have neglected to watch closely the advances we have made through scientific research."

"It will not take me very long to tell you what the textile manufacturing interests are doing to support technical research," said the laundry owner with a curious smile. "The manufacturers have allowed the consuming trades, such as the dry cleaners and laundry owners, to draw circles around them, and they, running around the circles, have arrived nowhere. Realizing the immense economic advantages of co-operation you have, it is true, organized your industry into trade groups, but this effort has not carried you far enough. You have not attempted on a proportionate scale the sort of research we have been discussing. Marketing research you are providing for, with machinery set up and financed by the trade groups, but technical research you have, in your short-sighted way, neglected. Better merchandising practice, more scientific distribution of products, control of prices and production, these the textile manufacturers have striven for, and laid stress upon, but in better products, more scientifically made, they have shown but slight collective interest. There are, of course, individual cases which are outstanding exceptions. I am talking of the industry in general.

"The exceptions are, primarily, a few associations that have been alert to the need for technical research and have shown their foresightedness by making use of the same facilities we consumers have used—the Mellon Institute and the Bureau of Standards. Those who have launched your research projects, however, have largely been the *technical* men of your industry, not the manufacturers. Your technical man understands the relation between his laboratory work and the ultimate sale of your goods better than you understand that relation, but his appeals have not, on the whole, been heeded. Where manufacturers have undertaken research of their own it has not always been systematic, has been too individual—not co-operative like that of the cleaners and laundry men; and not being systematic it has had slight effect on the industry."

"Has there, then, been no systematic technical research in my branch of the industry?" the Visitor asked gloomily.

"There has, to a limited extent, but you have paid scant attention to it. Some excellent work has already been carried out, mainly through the efforts of such bodies as Committee D-13 of the American Society for Testing Materials, the National Association of Hosiery and Underwear Manufacturers, and the American Association of Textile Chemists and Colorists. The last group has recently appointed a research associate to work at the Bureau of Standards, and has also worked with the apparel trades in suggesting fastness standards for fabrics. But these technical groups have been principally supported by their members, as individuals, who, in addition, have assumed the heavy task of planning their projects, down to the smallest detail. Encouragement from the industry in general for their labors has been mild, indeed.

"That is why the textile manufacturing industry has lagged so far behind the consuming trades in research. The best technical brains of the industry have come together to study ways and means of improving your products, but they have had to undertake their work in the face of severe handicaps created by your indifference. As the American Chemical Society once declared in an editorial in its journal, 'We grow pessimistic over the deaf ear which the American textile industry as a whole turns to the textile technologists and research workers. . . . There have been a few opportunities to establish a textile research institute in America, but they have passed either because of jealousies within the ranks of textile manufacturers or a lack of appreciation.'

"The mistake which you as a manufacturer have made," concluded the laundry owner, "has been in not capitalizing on the research that has been going on under your nose for several years. The vast difference between a few scattered, individual attempts at research, and systematic, co-operative effort has not been discerned by your industry. The result? The one or two groups which have approached your technical problems in the right spirit and in a truly systematic way have not been adequately supported. The achievements of the cleaners and dyers and laundry owners should contain a lesson, but so far it has escaped you . . . and now let me show you my laundry."

"No, thank you," the Visitor said, his curiosity for once subdued, "I have more important interests. I shall spend the remainder of my vacation in the laboratory of my mill to get a closer view of this research you have been discussing. My chemist can tell me what he and his fellow-workers have been doing for the manufacturers and perhaps tell me how I can help."

C. H.

John W. Russell, formerly chemist for the United States Worsted Corporation, has been promoted to the position of superintendent of dyeing and finishing and will be in charge of operations at their plant at Lawrence, Mass. Mr. Russell holds the degree of Bachelor of Textile Chemistry from the Lowell Textile School from which institution he graduated in 1920. He succeeds Everett S. Wells, who has resigned to accept a responsible position in Philadelphia.

Technical Notes from Foreign Sources

Producing Designs in Cellulose Acetate Fabrics

Effects or patterns are produced on fabrics which are made from or which contain cellulose acetate by the local application of a substance or substances which modify the delustering action of hot or boiling aqueous media or steam. Thereafter the printed material is subjected to the action of these agencies. The substances to be applied locally may be mechanical resists such as waxes, resins, gums, pigments, etc., or there may be solvents for cellulose acetate or subtances which dissolve therein, such as phenols, chlorophenols, aromatic amines or substituted amines. arylhalides, alkyl halides, aliphatic alcohols and phenols and cyclic bases.

Depending on the conditions these solvents or solutions may in some cases act to conserve the luster, while in other cases they accelerate the delustering action of aqueous media or steam. The solvents or solutes may be used in the form of aqueous solutions or pastes, or dissolved in non-solvents for cellulose acetate such as benzene, or xylene, or dispersed in aqueous media. The process may be applied to dyed or undyed goods; and since the delustered portions show a different behavior towards dyestuffs, differential effects can be produced by a suitable choice of the latter. Thus the delustered material shows a considerably altered affinity with respect to many water-soluble dyestuffs, such as Capri Blue, whereas delustering does not affect the rate of dyeing when employing the methods which are described in British Patents Nos. 219,349, 224,925, 242,393 and 242,711.

Furthermore, dyestuffs may be incorporated with the printing pastes. Other effects can be obtained in the case of mixed goods, for instance, such as have a warp of cotton and a weft of acetate silk. For example, printing pastes containing beta-naphthol, aceto-acetic ester or phenol, together with Turkey Red oil and a thickener, are applied to the fabrics, the goods are then dried either in a hot stove or at atmospheric temperature, and finally steamed. The fabric is printed with a resist which consists of molten rosin, and then treated with water at a temperature of 90 to 95 deg. Cent. (British Patent No. 266,777.)

Reserves on Vegetable Fibers

The new process for the production of these resists, as described in French Patent No. 597,611, consists in the alkalinization of the vegetable fibers by local treatment with the suitable alkalinizing means, such as a concentrated solution of caustic alkali, with or without any thickening agent, with or without the addition of alcohol or with an alcoholic solution of an alkaline alcoholate. Then the fibers are submitted in the dry or the wet state to suitable esterifying agents, such as the chlorides of carboxylic acids, the chlorides of sulphonic acids, or the anhydrides of the corresponding acids, these being either in the pure state or in solution. Then the fibers are vigorously washed after the reaction has been completed. The vegetable fibers, which are thus locally modified, can be dyed, in the ordinary manner, with substantive dyestuffs, without the parts which have been locally esterified absorbing any of the color. The result is that these places appear white on a colored ground.

It has likewise been found that in adding dyestuffs to alkalinizing reagents and in subjecting the fibers to a subsequent treatment with the aid of esterifying reagents, colored reserves are formed which are not affected in any manner by the subsequent dyeing operations.

On the other hand, it has been found that the reserves obtained in accordance with the process described above, by the local esterification of the vegetable fiber permit the dyeing to be carried out with the aid of basic dyestuffs, with derivatives of gallocyanin and with suitable acid dyestuffs. The result then is that the designs appear colored on a white ground. The fibers, which have thus been previously dyed, can then be cross-dyed with substantive dyestuffs, or it is possible to proceed in the reserve order, taking into consideration the possibilities of relative precipitation.

Crepe Effects with Colored Designs on Fabrics

There are different processes which can be used for the production of crepe effects on cotton piece goods in such a manner that it is also possible to produce simultaneously two-color designs in one and the same dyeing operation. The bleached goods are printed with suitable rubber reserve preparations and then dried. Then the goods are passed through a cold solution of sodium hydroxide, of approximately 52 deg. Tw. concentrated sodium hydroxide solution, are printed on the spots where it is desired to cause shrinkage of the fibers. When this has been done, the goods are washed, soured, washed again and dried. It is evident that it is possible by combining these two methods, particularly when using colored printing pastes, to obtain many varied effects in the fabrics.

If the problem is concerned with the treatment of mixed goods, that is, those containing cotton with wool or silk, then adequate consideration must be taken of the fact that the animal fibers are very sensitive to caustic alkalies. In this case advantage is taken of the fact, corroborated by experience, that the mercerizing action takes place so much quicker, the colder the mercerizing liquor. Hence, the process is

carried out at temperatures lower than 0 deg. Cent. yith a liquor of 52.6 deg. Tw. concentration. The action of the liquor must be allowed to last only for such a length of time that the creping action is produced. The washing of the goods is then carried out in cold water that is ice water. This step is absolutely necessary, as wool and silk are very easily attacked by caustic liquors which are greater than 10 deg. Tw. in concentration. It is best to carry out this process only in the winter months, and under these conditions the mercerizing action of the liquors has not the chance to injure the woolen or silken portions of the fabric. (Textile Recorder, through Der Textilchemiker und Colorist, 1927, No. 8, p. 58.)

Fast Dyeing Dress Fabrics

Dyeing with fast dyestuffs, that is with those that will give dyeings fast to washing and light, is very little practiced in dress fabric dyeing. It is, nevertheless, a field where fast dyestuffs should be largely used, for there are many complaints regarding the fading of colored dress fabrics and their slight resistance to washing, ironing, and other influences.

In the case of woolen and half-woolen materials, the dyeing should be carried out with the aid of good acid dyestuffs, and the after-dyeing can be carried out with direct dyestuffs. In order to save time, the materials are dyed with union dyes in a single bath, but when the dyeing process is not carried out in the proper manner and the goods are not properly washed, the result is a color that is apt to rub off.

In the case of cotton and linen fabrics, direct dyeing is not sufficient for the most part to meet the fastness requirements. Thus, such merchandise as cotton or linen house dresses, which are often washed, should not be dyed with direct colors, for they do not stand up against the action of soap and water.

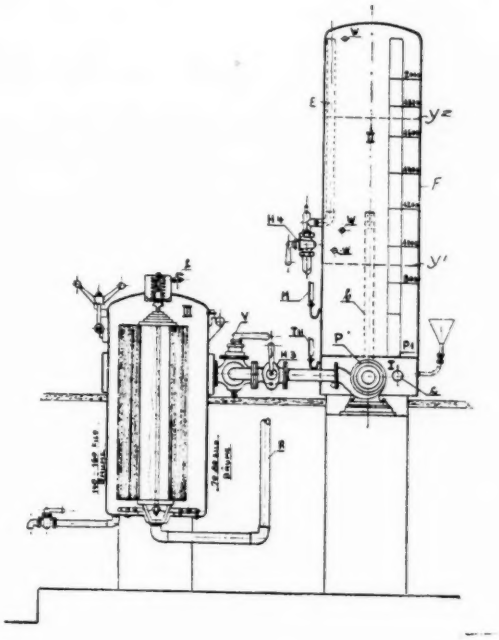
There are a number of substantive dyestuffs which have at least a good resistance to light. Every dyestuff manufacturer publishes information regarding the fastness of his dyestuffs, and it is possible to choose the proper ones for this purpose.

Only blue and black of the developed benzidine dyestuffs are of importance in dyeing dress fabrics. Thus, among the blues may be mentioned Diaminogene Blue, NA, 2RN, 3RN, etc., and among the blacks Diamine Black DB, DN, Oxydiaminogen ED, etc.

All these dyestuffs yield results of good or very good resistance to light, quite good fastness to washing, and excellent resistance to perspiration. The goods should be preferably dyed in a stationary liquor. In the diazotizing and developing process, wooden vats are employed. (Deutsche Faerber Zeitung, 1927, p. 396.)

Dyeing Warp Yarn

German Patent No. 436,670 describes an apparatus which is used for the dyeing of warp yarns with the aid of a circulating liquor, the apparatus being provided with a color or liquor container. The apparatus can be used for dyeing the lighter and the heavier yarns as well, but the quantity of dye liquor used will, of course, vary in accordance with the character of the yarn, although there will be no loss of dye liquor. The loss of dye liquor is prevented by running a pipe from the color container to the liquor container, and this pipe opens out at various heights in the liquor container. For example, if a light warp beam is brought into the dyeing chamber, then the dyeing is carried out with the lowest opening in the pressure tube, and only a comparatively small amount of liquor is required for the operation. On the other hand, if a heavy warp beam is being treated, then the dye liquor is allowed to flow into the dyeing chamber through higher openings in the pressure tube.



The apparatus is shown in the accompanying illustration. The dye container III, which is made in sufficient width, is connected with the pump P by means of a four-way cock V, and the suction pipe connection of this pump leads from the compartment I of the liquor container F. The pressure pipe of the pump is divided into two parts behind the four-way cock V, and one of these branches opens out into the lower chamber and the other into a higher portion of the liquor container F. If a light warp beam is in the dyeing container or vessel III, then the valve H_3 is so adjusted that the liquor is taken only from the lower portion of the liquor container. On the other hand, if a heavy warp beam is being dyed, then the valve is so adjusted that the branch pipe which opens

out into the upper portion of the liquor container is connected and a considerably greater portion of dye liquor is placed in circulation.

Treating Material Dyed with Sulphur Colors with Sodium Bisulphite

It has been found that by treating material dyed with sulphur colors with sodium bisulphite, that it is possible after dyeing to obtain the color tone which the dyed material assumes after slow oxidation. Hence, the use of sodium bisulphite is more advantageous than that of alkali sulphites, for it is unnecessary to dry the material in order to obtain the desirable effect and because the fabric can be washed after the treatment.

In an example, the fabric dyed with one of the sulphur colors was washed and then treated with a cold fresh solution containing from 2 to 3 per cent of sodium bisulphite of 40 deg. Be. concentration. (Bulletin de la Societe Industrielle de Mulhouse, 1927, p. 12.)

Rayon and Silk Handle

A soft handle on taffetas is obtained by washing the goods after dyeing and brightening with a 3 per cent solution of the brightening acid, 5 per cent of diastafor and ½ per cent of olive oil. The oil is first boiled up with a little soda in the usual manner. The temperature of the solution should be maintained at 35 deg. Cent., and twenty minutes are required for the treatment. Then the liquor is allowed to run off, the material is centrifuged and dried.

A delicate handle is obtained by treating the material, according to its character, with 5 to 10 per cent of brightening acid, plus 0.2 per cent of Marseilles soap and 5 per cent of diastafor, as well as ¾ per cent of olive oil, prepared as heretofore. A somewhat more delicate handle is obtained by the addition of a little bast soap to the brightening liquor, for example, 10 per cent of acid plus 20 per cent of bast soap plus 5 per cent diastafor and 1 per cent of the treated olive oil. (Kunstseide, 1927, p. 275.)

The Differentiation of Viscose from Cuprammonium Silks Through Color Reactions

The Naphthalamin Black Test—Experiments of Rhodes and Gotze—The Results Tabulated

By PROF. P. KRALS

(Translated from Der Papier-Fabrikant by Dr. Paul Bartholow)

THOUGH viscose silk of very fine fibers has recently appeared in commerce, the microscopical tests hitherto regarded as sufficient are nevertheless not adequate to the purpose. For while the single fibers of viscose silk commonly possessing a strength of 7-8 den., owing to their much greater thickness, and longitudinal striation, may be easily distinguished from the smooth cupra silks of only 1-1.2 den., the fine new viscose silks show no longitudinal striation, or only a very incomplete striation.

The determination of nitro silk by means of the diphenylamin-sulphuric acid reaction, and acetate silk by its solubility in acetone or acetic ether is indeed easy, but for the differentiation of cupra and viscose silks there has been so far only one simple and sure color reaction, namely, coloration with 4B Naphthylamin Black in a hot neutral bath, as recommended by the firm of Cassella & Co. By this means cupra silk is colored dark blue, while viscose is colored a lighter, usually a pinkish blue. A few years ago the author drew attention to this reaction, and at the same time as equally simple and in many instances (especially when we are handling dyed fibers) equally sure, the examination of a cross section under the microscope. But, as indicated above, the method in the case of very fine fibers of viscose silk may leave the investigator in doubt. It is therefore a matter of satisfaction that this problem has received fresh attention. For example, K. Gotze[1] has found that treatment of viscose silk with heat and a 1 per cent solution of ammonio-potassium silver nitrate is followed by a distinct brown coloration of the fibers, whereas cupra silks remain uncolored. Similarly O. S. Rhodes has commended a reaction which he states gives an even clearer differentiation, namely, boiling of the sample for a minute in a solution which contains 1 per cent silver nitrate, 4 per cent sodium thiosulphate and 4 per cent caustic soda. The solutions are made separately, boiled and filtered. Rhodes compared the brown color obtained with both solutions with that of Chlorazol Brown M (probably identical with Diamine Brown), and found—especially in the case of vistra silk—that the color obtained by means of his reagent gives a much deeper shade (4 per cent compared with 1 per cent) than that obtained with ammonio-potassium silver nitrate solution. Rhodes mentions that the thiosulphate silver solution had previously been used by W. Harrison as a reagent for oxycellulose. In this instance a gray, not a brown, color followed.

I have compared the three reactions in the following manner: The samples of artificial silk shown on the subjoined table were heated a minute to boiling in both silver solutions which were then poured off; the two sets of samples were next washed with water, and the colors

compared under water in a test tube. Moreover, the coloration with Naphthylamin Black was produced by wetting the sample with a 1:2000 solution of the dyestuff; it is then kept immersed half an hour in a boiling water bath, taken out, washed and examined under water.

	I. Rhodes	II. Gotze	III. Cassella
1. Viscose silk, 7-8 den.	Very dark black brown	Dark brown, opaque	Light gray, reddish
2. Viscose silk, 4 den.	Black brown, lighter	Dark brown, opaque	Light gray, reddish
3. Viscose silk from linters, 7-8 den.	Black brown, still lighter	Clear dark brown	Light bluish gray
4. Cupra silk, 1-2 den.	Gray, very light	Light yellowish brown	Dark bluish gray
5. Nitro silk	Black brown, very dark	Opaque brown	Bluish gray, reddish
6. Acetate silk	Bluish black	Light brown	Light gray, reddish

According to my own impression, the difference in color in I, especially in the Samples I to IV, which are the most important, is more distinct than in II; moreover the difference in III is at least as distinct as in I, and more distinct than in II. It is perhaps preferable not to boil II, but to heat only for a short time. It is interesting also that sample III of viscose silk prepared from linters remains quite clear, and this sample gave a dark color with cupra silk only. The question as to what causes these differences in coloration is to-day not capable of an unexceptionable answer.

REFERENCES

[1] Textile Forschung, 1920, p. 64
[2] Jour. Textile Institute, 1926, p. 75.
[3] Jour. Soc. Dyers and Colorists, 1912, p. 361.

Practical Hints on the Production of Bright Colors on Textile Fabrics

Part XXX

Most Suitable Topping Colors and Combinations—Other Factors in Brightening the Shade—Drawbacks of Jig Dyeing—A Plant with Submerged Rollers—Its Construction and Operation

By RAFFAELE SANSONE

WHEN topping was conducted for the first time on cotton fabrics dyed with sulphur colors, any basic dyestuff of the same color was used, it being the principal aim to brighten with as little change of shade as possible, also to assist the matching operations. At present the dyer goes farther and essays to enhance the more or less dull sulphur colors by a strong contrast; by placing, for instance, a green or a yellow with a blue, a pink or violet with a blue, a pink or red with a blue, an orange or red with a yellow, a green with a yellow, a yellow with a green, etc. Some effects are also obtained by performing a first topping with a basic blue and a second with a basic yellow, a first topping with a basic yellow and a second with a basic blue, or a first topping with a bright basic pink and a second with a basic yellow. In this way a ground brightening is first obtained, on which the amount of the contrasting color is increased or reduced and can also act as a shading means.

Through a similar arrangement very fine results are possible. Besides the above variations, the basic colors used are of lighter shade than the sulphur colors, or of about the same intensity of shade or much darker. In all cases special care is necessary for using just the products which will give the best results with the sulphur dyestuffs employed or available. Some basic colors are therefore to be preferred to others, the more so that the number of the topped shades and effects at present produced is quite large.

The choice of the sulphur colors used for preparing the ground or principal color plays a very important part in obtaining the finest shades, for some of them possess a better brightness than others and can assist halfway the action of the topping colors. Besides this, if several products are used for producing a given shade not possible with a single color, they should be carefully chosen with the idea of always enhancing the shade, and in some cases it may be convenient to leave out a sulphur color in a mixture when a basic color can replace it to advantage. To obtain certain shades it may be more advantageous to employ sulphur colors which are steamed, while for others a similar principle need not be adopted, as the ordinary oxidation in the air will be sufficient.

Other Factors in Brightening the Shade

The sulphur colors, however carefully they are chosen, cannot give the very best results if other factors of great importance are not considered, such as (1) the condition of the material treated; (2) the qual-

ity of the chemicals used during the dyeing operations; (3) the way the dyeing is conducted, etc.

Cotton cloth, to allow the production of the brightest shades, should be of a pure white and without any bluing agent. If it is left with a dirty cream color this will reflect across the colors dyed, dulling them to a certain extent. Mercerization can be used to assist the brightness by a strong luster, and in this case the construction of the cloth itself can be of assistance, as can also the final finish given to the goods. The quality of the chemicals used in the dye baths is another very important factor to be considered. The writer has often observed a difference in two separate lots of cloth which have been dyed with the same colors, where one resulted duller than the other, not through any fault of the dyer but simply as a consequence of the use of dirty sulphide of soda, carbonate of soda or salt. These contributed toward spoiling the beauty of the shade, rendering its correction quite impossible.

For the above reasons the very cleanest products must be used. It is well to conduct small laboratory trials in this case, where samples of bleached calico are treated in solutions of proper strength of the sulphide of soda, common salt and carbonate of soda or caustic soda to be used on a large scale, to control the degree to which they are colored. Should a pronounced coloring result, a demand for cleaner products must be placed with the makers of such products. It will also be useful to treat a small sample of bleached cloth in the dye baths before adding the dyestuff, to determine how the shades will be altered during the dyeing.

Another factor of great importance which has its influence in the production of the brightest shades is the way the dyeing is performed with the sulphur colors, as these can often be spoiled or dulled through lack of the necessary precautions. It must not be forgotten that when the desired intensity of shade has been produced, the baths are anything but exhausted and an excess of color can easily be deposited on the dyed fabric, remaining imperfectly fixed and often giving a bronzy appearance. This deposit of superfluous color must therefore be avoided.

In some works, when dyeing in the jig, the best result is reached by placing such machines in pairs, using one of the jigs for the dyeing operations and one for the rinsing. In this instance, when the desired shade has been produced the cloth is run at once from the dye bath to the rinsing water, while this is being rapidly changed and a multiple spraying is being applied on both sides of the fabric. All dye liquor still present on the fabric is thus rapidly washed out before the color it contains has the time to become fixed, the action of the water sprays going right into the innermost cells of the material. The arrangement leaves the dyed goods with a clearer appearance and much faster to washing and soaping.

In some works the jigs employed are supplied with two pairs of squeeze rollers, which press the material before it passes into the rinsing bath, thus reducing the quantity of dye liquor to be eliminated. With some colors, however, it is necessary to finish off the rinsing with a weak soaping by using a special plant.

Dullness can result in some cases through an imperfect solution of the sulphur dyes, caused by the use of too little sulphide of soda. It must not be forgotten that this product, if left in contact with the air, absorbs moisture and loses strength. Some dyers are convinced of this, for as soon as they receive the kegs of the product they empty out their contents into glass-lined deposit cases, which are sealed hermetically, and take out enough for immediate use. A similar precaution is well worth taking, as it guarantees a greater constance in the dyeing operations, especially if the product is obtained from a reliable manufacturer.

Another wise practice is to sieve the dyestuff solution into the dye bath. In this way any insoluble portion which remains can be dissolved in further sulphide of soda solution. If this is not possible, the residue is probably ordinary sand or other insoluble mineral powder which has fallen into the dry dyestuff or has been added in packing. The above does not mean, however, that a large excess of the sulphide of soda should be used in the preparation of the dyestuff solutions, nor that the quantity of this should be maintained equal in all cases, as some dyes require more of the product and others less. Matters should be arranged, however, so that a certain excess of sulphide of soda is always present in the dye bath, as this helps to assure clearer shades and facilitates the thorough fixation of the colors.

Defects of Jigger Dyeing

Although sulphur colors are largely dyed on the jig and the results obtained satisfy many purposes, the ordinary type of machine employed in the majority of dye works offers the following disadvantages:

1. The cotton cloth is imperfectly oxidized.

2. It is dyed unevenly during the repeated oxidation out of the bath.

3. A portion of the dyestuff fixed on the material at the beginning of the dyeing is reduced and extracted later, retarding the dyeing somewhat.

During the winding of the cloth on the roller on the right of the jig or on the roller on the left, the first portions are exposed for a longer time out of the dye bath than the rest, and especially than those coming out last from the dye bath, which during the dyeing operations re-enter the dye bath after a very short interval of exposure. It is true that the portions exposed longer the first time are exposed less the second when wound on the roller at the opposite end of the machine. The action of the dye bath is, however, already weaker. Besides this, the middle of the piece

is exposed in a manner different from the beginning or end.

Although in practice these troubles pass unobserved, and the great strength of the baths employed and the skill of the dyers prevent to a certain extent differences which may follow between the various portions of the pieces dyed, there is no doubt that in many cases they are the cause of claims on the part of unsatisfied clients or of reducing the profits of the dyeing. Such troubles are lessened in some works by using dyestuffs of easier or more rapid oxidation which are already fixed completely by the time the cloth reaches the winding roller, which therefore only serves for moving forward. The baths are also furnished with just the quantity of sulphide of soda necessary to keep in solution the sulphur colors. The arrangement, however, cannot be applied to all cases, and especially to those where it is desired to produce the brightest effects. When the jig runs at considerable speed, the dye liquor taken up by the cloth remains in it in abundance and continues to make its way to the lower spirals on the winding rollers. A portion of the goods is thus impregnated with more bath than the rest and retains a larger quantity of oxidized dyestuff.

A Plant with Submerged Rollers

To assure a uniform distribution of the dye bath in the different spirals of the cloth wound on the rollers of the dyeing machine, the rollers are kept below the bath, as shown in Fig. 1.

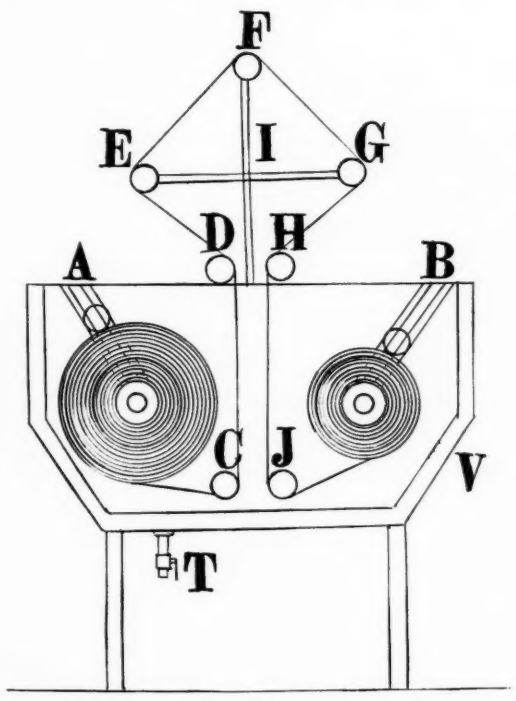


Fig. 1

This illustration shows a plant consisting of a large iron vat V of special shape and kept at a short distance from the floor of the mill by four strong iron legs. Vat V is furnished with a large tap T for the discharge of all dye baths, and its shape just permits the winding and unwinding of the cloth between two porcelain cylinders at a short distance from one another. Such cylinders are fitted in bearings arranged in the walls of vat V and are turned by a special arrangement on the outside so as to cause the cotton fabric to run continually from one cylinder to the other, the movement being reversed automatically whenever one of the cylinders has been filled and the end fixed on the roller being emptied causes pulling. The bearings used in this case are water-tight and no loss of bath can follow.

Two pairs of inclined guides (A and B) are furnished to contain the short end-shafts of two small rollers resting by their weight on the cloth being wound on the lower cylinders. Above vat V are fixed two light iron frames (I) which sustain the five guide rollers D, E, F, G and H, turning freely and noiselessly in ball-bearings. The cloth is led to such rollers by the two rollers C and J.

At the bottom of vat V is placed a long, closed, glass-covered iron coil, by which the different dye baths can be rapidly heated with steam entered from a tap placed on the outside, while all waste water is eliminated by a small steam trap. The arrangement turning the cylinders for the winding and unwinding of the goods is furnished with two speeds, a slower for the dyeing operations and a more rapid for expelling liquid whenever this may be necessary, the speed being changed by means of a short hand lever.

With the idea of assisting the continual movement of the baths across the rolls of goods on the winding and unwinding cylinders, these are perforated at regulated intervals over their round surface and are hollow in the inside, which remains under the alternated action of aspiration and pressure produced by a small apparatus worked without a pump and which causes only a small movement in the inside of the cylinders themselves sufficient to cause the baths of treatment to continually fill and empty the rolls while passing through the cloth.

Work on the Plant

The operation of the above plant is not complicated. The operatives attach to the winding shaft on the left the end of the first roll of fabrics to be dyed, and wind this entirely on the shaft by starting the driving mechanism. When this has been done, they cause the loose end of the cloth to pass below roller C and carry it upward to roller D, bringing it then around rollers E, F, G and H, below which it is pulled to roller J and fixed to the empty cylinder on the right.

After the entrance of the cotton goods the dye bath

is prepared in a separate kettle and entered in vat V. It should entirely cover the fabrics being treated, passing above these for about 2 or 3 inches. At this point steam is turned on in the coil at the bottom of vat V to bring the bath to the boil and the cylinders are started to move the cloth forward from left to right. In this way it is wetted through rapidly and mounts to the exposure frames I to be oxidized, re-entering the bath to pass on the empty cylinder.

As spiral after spiral is wound on the cylinder, it remains continually soaked with the dyeing fluid, which is forced in and out by the action of the suction and pressing device. In this way, after several passages the desired shade is produced and the dye bath can be run off and replaced with clean running water, which is caused to enter at the top and pass out through tap T, while overflowing also over the upper walls of vat V. The movement of the cloth is then continued for some time with the pumping apparatus continually in action, after which all water is turned off and the cloth allowed to run entirely on the roller on the left, which is caused to revolve at the highest speed of the machine to eliminate the greater portion of the liquid it contains and prepare for the drying operations.

Advantages of the Plant

The plant possesses the following advantages:

1. The cotton cloth, impregnated with the dye bath, is oxidized continually and always in the same way, quickening the production of the desired shade, with the possibility of reducing the quantity of dyestuff and sulphide of soda necessary in the bath.

2. Through the submersion of the wound and unwound cloth, and the forced passage of the baths of treatment, penetration is most rapid and thorough, and there is no danger of dyeing one portion of the material more intensively than another, even if the baths contain a smaller quantity of dyestuff than generally employed on ordinary jigs.

3. The possibility of eliminating all excess of liquid on the machine itself avoids the use of an extractor without much reducing the production.

4. The dimensions of the plant can be varied in accordance with the scale of treatment, as through the continual forced passage of the baths across the rolls of cloth there is no danger of unevenness.

Re-Solution of Fixed Dyestuff and Irregular Speed of Treatment

On re-entering the dye bath each time a portion of the dye fixed on the cotton cloth through oxidation is extracted, especially if the bath contains a large excess of sulphide of soda; and even if this is compensated for by the new lot of dyestuff solution taken up when rolling out of the bath, it contributes toward increasing unnecessarily the time required for the dyeing. For such reasons there is a tendency to seek plants in which this inconvenience can be eliminated, or at least reduced or brought under conditions that do not interfere with the speed of the process.

On many ordinary jigs the speed of the cotton fabric passing through the dye bath increases more and more as spiral is placed over spiral on the winding cylinder on the outside. It follows that the end of the cloth when run from right to left remains longer in the bath than what follows, although just the contrary should take place through the gradual absorption of dyestuff. When the cloth returns on the road made and is rewound on the roller at the opposite end of the jig, the seed is reversed and that part of the goods treated more slowly which before were treated rapidly. For the above reasons, to get uniform shades it is necessary to give the cloth two or four ends, and not three or five, and to keep the bath always much above the concentration really necessary for the desired shade.

To overcome the above features and those previously indicated, jigs with two pairs of squeeze rollers have been adopted, in which the cloth is treated continually as it comes out of the bath of treatment. In this way the quantity of bath oxidized in the material remains always uniform, and too little liquid is left to cause an excessive wetting of the covered spirals during the dyeing operations. Besides this marked improvement, the speed of the passage through the treating fluids remains the same in all cases, since the pull on the cloth is equal at all moments of the dyeing. In this case, however, the difference in the time of oxidation is not reduced and remains about the same as with ordinary jigs, while the re-solution of a portion of the oxidized and fixed dyestuff still continues. A plant in which the re-solution is greatly reduced and all other inconveniences avoided altogether, while the production is very satisfactory, is constructed on the principle shown in Fig. 2.

This is composed principally of three dye jigs placed in a straight row, one behind the other, and of a rinsing and soaping arrangement for treating three lots of cloth at one time. The jigs have a dye vat V which is square in the lower half and funnel-shaped in the upper. The material used in the construction of this vat is specially chosen to resist the action of the different baths of treatment and can be easily cleaned. On the bottom is placed a large discharge tap, so arranged that every drop of liquid can be withdrawn into lower cement collection troughs or into the waste water main.

The interior of vat V contains four lower and five upper binding rollers, of small diameter, to reduce the space occupied to the lowest possible limits. Above this vat is placed a pair of strong iron frames having two vertical arms with central slots for the short end-shafts of the pairs of squeeze rollers a and b, which are turned in ball-bearings by the assistance of pulley P. The squeeze rollers remain under a slight pressure, regulated by springs and upper screw-wheels. Two pairs of inclined

arms are furnished, each carrying a roller. That before rollers a is surmounted by a cloth opening device O, while that after rollers b serves principally for passing the dyed cloth to the rinsing and soaping plant. The jigs are supplied with a special automatic movement, through which each dyed portion of the cloth is moved three times backward and forward in vat V before being delivered out of this, the same movement being performed on device O and on the rinsing and soaping plant. The side at which the movement is to be started first is regulated by turning one of the hand-wheels at each end of vat V.

The rinsing and soaping plant consists of three long narrow iron vats, each divided into four compartments A, B, C, D, lined with thick glass and supplied with several upper and lower binding rollers and the pairs of light squeeze rollers indicated by c, d, e, f. The first two compartments of each vat are for conducting a very rapid and thorough rinsing with water, entered from a lower perforated coil and making its way out at the top through overflow perforations. The third compartment, C, is used for conducting a weak soaping with a bath of running water, the goods passing less quickly than in compartments A and B, in which a stream of strong soap solution is entered by tap U from the upper half tub T, in such a manner as to come in contact with the dyed cotton fabrics only when well mixed with the bath of treatment. Compartment D serves for a last rinsing with water, circulated in the same way as with compartments A and B.

The whole of the three vats are surmounted by a light wooden frame F, having at the top a platform which is mounted by the operatives when preparing the soap bath in the half tubs. At the beginning of frame F is simply a guide roller, by which the tension is regulated on the fabric being treated. At the end of framing F are two projecting arms, where the dyed, rinsed and soaped cotton fabrics are spread out on a small wagon or truck ready for delivery to the drying department or wherever else may be necessary for further treatment.

All movement on the rinsing and soaping plant is regulated with that of the three jigs, the cloth being carried even in this case backward and forward for three times while being brought forward continually for a fixed interval. The bath in compartment C is heated, if necessary, by a closed steam coil at the bottom.

Operation of the Plant

Operation of the above plant would be as follows: A cotton tape is passed through the jig and rinsing and soaping apparatus, sewing to its end the ends of the pieces of cotton cloth to be dyed, which have been properly wet out on a separate plant. The strong dye baths are then prepared in three kettles at the back of the installation, entering a fixed volume of salt solution, of convenient strength, in the vats of the jigs, with or without soda as may be necessary.

When the above preparatory operations have been performed with the usual precision and diligence, the dyer enters in each vat, by means of glass-lined iron dippers, the strong dyestuff solution, mixes rapidly with a dye stick and starts the plant. In the meanwhile another operative has turned on the nine rinsing baths in the vats of the rinsing and soaping plant and the water in the three soaping compartments, entering in the last a fixed volume of the soap solution and regulating the inflow of this through the taps U, keeping always at the same strength.

As the cotton fabric enters between the nip of squeeze rollers a, the operatives watch that no plaits pass forward, placing themselves for this purpose before the opening arrangements. On entering the dye baths, the three lots of cotton cloth rapidly take up a first charge of color, which during the course upward to the nearest binding roller is fixed by a short oxidation. After this the impregnation and oxidation is repeated three times and the cloth is delivered between the nip of the squeeze rollers b. The automatic movement, regulating all work on the plant, now comes into action and brings the cloth backward and forward three times, after this delivering the portion dyed to the rinsing compartments, while preparing a second, a third and following portions in the same way with the dye bath.

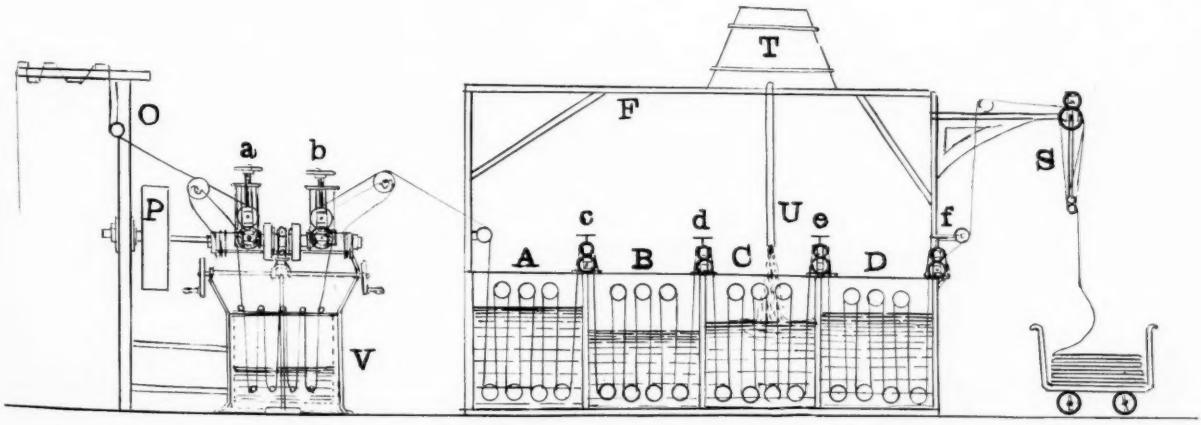


Fig. 2

In this way yard after yard of the wet cotton goods is colored continuously in the different baths, and after a time the operatives enter more dyestuff and salt solution in each vat to keep this always of the same strength. On entering the first two rinsing compartments, A and B, the dyed goods pass three times backward and forward in the rapidly mounting water, which not only eliminates all mechanically fixed dyestuff but also completes the oxidation of that more strongly fixed in the material. In the soaping compartments indicated by C, the three lots of cotton cloth are passed three times backward and forward in the weak soap baths, being treated with the same energy as on many of the ordinary soaping plants. In the last compartments indicated by D, a last rinsing is conducted in exactly the same way as in compartments A and B, so that each portion of the material, on leaving this, makes its way with very little soap to device S to be spread on the small wagon.

Special Features of the Plant

The above plant possesses the following advantages:

1. Three separate lots of cotton cloth are dyed continuously in the same, in two or in three colors, with a minimum employment of labor, steam, dyestuffs and chemicals.
2. The time the fabrics remain in the different dye baths is sufficiently long to produce the darkest shades.
3. The cotton goods are entered in piece form and delivered dyed, rinsed and soaped in the same form.
4. The three jigs can be worked at once, or only one or two at a time, so that while a new bath is being prepared in one, dyeing operations can be continued in the other two.
5. The special form of the dye vats allows the use of short or long baths.
6. The speed of the passage of the cloth in the dye bath is always the same, and so is the oxidation and contents of dye liquor left in the goods after leaving the jigs.

(*To be continued.*)

GERMAN DYESTUFFS PRODUCTION FOR FIRST QUARTER, 1927

The statistics for the first quarter of 1927 show that, evidently without detriment to the domestic market, exports from Germany of the more important synthetic dyestuffs have increased. Aniline, tar, and sulphur dyestuffs exports were 6,963 metric tons as compared with 4,957 in the same period of 1926. The relative increase in alizarine dyestuffs was even greater, having been 1,235 tons, as compared with 272 tons. Indigo was exported to the amount of 4,517 tons, as compared with 3,942 in the first quarter of 1926. Heavy competition in Indigo by three American companies has been mentioned in Frankfort lately, principally with regard to the Japanese and Chinese markets. Apparently not only the Germans but also the Swiss are affected by this competition.

RECENT LITERATURE

CORRECTION

The publication of "Colloid Symposium Monograph" was erroneously credited in our issue of June 13 to the D. Van Nostrand Company. This monograph is published annually by the Chemical Catalog Company, of New York.

A Standard on Cotton Dyeing

The Dyeing of Cotton Fabrics. By Franklin Beech. Third edition; revised and enlarged by A. J. Hall, B.Sc., F.I.C. D. Van Nostrand Company, New York. 296 pages; illustrated. $5.00.

The first edition of this work was issued over a quarter of a century ago and as it has gone through two revisions since then it can supposedly be regarded by now as a standard.

The revisions embodied in this new edition have been made principally to bring the book up to date rather than correct any of its original material. To the text of the second edition has been added considerable information relating to vat and sulphur dyes, the dyeing of rayon and some of the newer machinery employed in textile processing.

The production of sulphur dyes, of course, has been developed as one of the major branches of the dye industry, both here and abroad, but the changes recorded have not been nearly so extensive as the changes in the *application* of that class of colors. Similarly, the vat colors and their application represent one of the most rapidly advancing phases of the science of dyeing. Hence it has been necessary, in revising texts of all old books on dyeing, to enlarge and amend the chapters on dyestuffs to include the latest data on vat colors and, in the case of cotton dyeing, on sulphur colors as well. At the pace at which dyeing methods change, such revision seems to be necessary every five years.

Dyeing machinery construction has also moved forward with the development of dyeing methods—has often brought about new methods, in fact. Several new pieces of equipment are described in "Dyeing of Cotton Fabrics," and these offer evidence of the advances made in the mechanical branches of dyeing in the past decade.

The remainder of the text, opening with a chapter on the structure of the cotton fiber, deals with every operation in cotton processing, from bleaching to every class of dyeing, with special chapters on union fabrics and rayon, the latter comprising new material. Three chapters, on the operations following dyeing, on color testing

of dyed fabrics and on experimental dyeing, conclude this readable and ever-useful volume.

Textile Education

The Pennsylvania Museum and School of Industrial Arts —Circular of the Textile Department (Philadelphia Textile Schools), 1927-1928. 138 pages; illustrated.

The contents of this well-arranged bulletin should give every reader interested in textile education a great deal to marvel at. Perhaps among his files one may find a dusty copy of an early issue, one published, say, twenty or thirty years ago, giving a sketch of textile education as it then was, when the Philadelphia Textile School was building its reputation. A comparison of the educational facilities offered even ten years ago with those available to-day is enlightening. The training of each generation of textile engineers and chemists has had to keep pace with, or in advance of, the development of textile manufacturing.

This bulletin comprises full and detailed information about the Philadelphia Textile School, its officers and staff, its admission requirements and its many courses of instruction. It is illustrated with some very interesting photographs of the classrooms and laboratories and of some of the students' work.

Tanning with Paper Mill Waste Liquor

Use of Sulphite Cellulose Extract as a Tanning Material. By E. L. Wallace and R. C. Bowker. Technologic Papers of the Bureau of Standards, No. 339. Illustrated.

An investigation was conducted to determine the suitability of sulphite cellulose extract, derived from the waste liquors from paper pulp mills, for use in tanning hides. The work included an analysis of various extracts for tannin content in comparison with vegetable tanning materials. Information regarding the combination of tannins in these extracts with hide substance is presented, derived from actual tanning tests on both hide powder and pieces of raw hide.

The results showed that these extracts contain materials absorbable by hide powder in quantities which compare favorably with the amounts found in the ordinary vegetable tanning materials. Tanning tests on light skins showed that the extracts are satisfactory so far as color is concerned. It is concluded that sulphite cellulose extracts are suitable for use in the actual tanning processes, and that the tanner may benefit from their use to the extent that they may be substituted for more costly materials. Their use also is of direct advantage to the paper-pulp producer, in that it will aid in solving his waste-disposal problem.

CO_2 Meters (Electrical); Bulletin No. 781. *Galvanometers.* Leeds & Northrup Company.

Those who use instruments for CO_2 measurement as a guide to efficient boiler operation will find much instructive data in the bulletin describing the construction and operation of an electrical CO_2 meter developed by the Leeds & Northrup Company. The contents are in the nature of a technical treatise on control of combustion, effect of hydrogen in fuel and similar topics. The bulletin is illustrated in color with diagrams and charts.

The catalogue on galvanometers is equally well arranged for quick, convenient reference, with numerous cuts of various types of the instrument and its accessories, and notes on their use and design.

The Dyer's School of Experience

[EDITOR'S NOTE.—*The following narrative is one of a series being published under the general head of "The Dyer's School of Experience." Realizing that the genuine material for such a series is to be found largely among its own readers, The* REPORTER *solicits contributions from that source and will pay for those accepted at regular space rates. Among the readers of this journal there should be many who have, in the course of their experience as dyers or chemists, encountered incidents which should prove most interesting and helpful to their fellows. Send all manuscripts to* AMERICAN DYESTUFF REPORTER, 90 *William Street, New York City.*]

A CIVIL WAR IN A SILK MILL

By NOEL D. WHITE
Davenport Hosiery Mills, Chattanooga, Tenn.

THE first two years in the new Canadian silk mill were spent in building up a good trade.* We had by now a reputation, and business was as good as could be expected.

I had met the president and sales manager one morning after he had come back from a cross-continental trip—a very successful trip. He had come in to the mill soon after I and had asked me if I were the new dyer. When I answered in the affirmative, he told me to go out and pay the cabman who had brought him from the station. "Why," I said, "I do not know whom you are and what business you have here." He introduced himself, saying he had just come back to town and wanted to get some things before he went to the hotel. He told me he had heard of my work and was glad I was here with them to help build up the business, and that the prospects for the future were very good.

Later, when I spoke of him and his actions to the manager, he said that the president had probably lost all his money playing poker on the train from Vancouver. He was a tall, handsome man, built like a Greek god; of the Jewish persuasion, a pagan by in-

*In the previous instalment the author told of securing a position in a silk thread mill in Canada, lately established.

clination. As good a salesman as there was in the country, but wine, women and song exhausted all his earnings. He could go out and sell the production of the mill for three months in advance and come back from the trip with his earnings overdrawn the first week. He was the despair of the manager, who was thrifty and industrious, quite his opposite. However, both were scrupulously honest in their dealings.

There was in Canada in those days only two other silk mills to compete with. Both were branches of bigger mills from the United Sttaes. At first they paid no attention to us, but when they saw their trade impaired by our inroads among their customers they began to take notice and to find a way to curb our ambitions.

They did a lot of advertising in the trade papers, and my boss did not advertise at all in the beginning, leaving it to the salesmen to bring our silk to the tailors and dressmakers. After we put out our new shade card with 108 shades on it we had some cabinets made and placed in department stores, and also started advertising our brand of sewing silk. Naturally, that brought more business and also made our two competitors come together to see what could be done.

My boss was invited to meet the representatives of the other two firms one evening at a hotel. He got in touch with the president and asked him to return to Montreal to attend the meeting with him. The following morning I was told the result of that meeting.

Briefly, the two competitive mills had offered to buy out our mill and close it. Then, when my boss refused to sell, they offered a sum of money to make us discontinue the making of colors for the yards trade. That meant the silk we put up in 50 and 100 yard spools for the dressmakers and department stores.

The president, at the prospect of making quick and easy money, was ready to take up their proposition; but the manager reasoned that if it were worth any money to the other party to make us quit it was surely worth more to him to keep it up. He said that the president could, if he desired, sell his share in that part of the business, but that he was going to keep his works going. Nothing came out of that meeting except a resolution on the part of the manager to try for the control of the business, that it might not be jeopardized through the short-sightedness of his partner. That could be brought about by buying out the shares of the silent partner in New York. He started inquiries in that direction, but it took some time and a lot of tact to bring it about quietly.

In the meantime we pushed the making and sale of the yard thread. In every city and town in the Dominion show cabinets with our silk brand found a place in one or more stores; more sample cards were distributed to the dressmakers and milliners in the entire Dominion, and our business grew fast.

Of course, the refusal to sell out to our more powerfu! competitor started a war in prices which our firm would not have been able to carry on except that our way of loading the silk, about which I doubt that the other firms knew at that time, helped us to meet their prices and make a profit besides—so the war didn't last long.

One day the manager came to tell me he could get a contract for three months' supply of white silk from a shoe manufacturing concern if I could load it at least 2 ounces to the pound. We had not attempted to load the white because there was so little of it sold until now. He did not see how it could be done. I told him there were several ways and that I would make a trial on 5 pounds with a solution of loaf sugar, another with glucose and gelatine, and still another with bichloride of tin, if I could procure it in the city. Then he could select the one he preferred. He was elated over the idea and told me to go ahead.

I bought a 4-gallon crock and a bowl. Then I went to the chemical house from whom we bought our chemicals for the dyehouse and asked them to find a few gallons of bichloride of tin for me. They had one carboy at hand, and I found out that one of our competitors, who was also manufacturing ribbons, was making experiments in loading the tram for that purpose. I made up my mind to make the acquaintance of the dyer in that place and find out what he knew about loading silk.

As I have mentioned before, I knew practically all that was known in those days about how to load silk, but I was curious to find out how much of that knowledge had gotten through to Canada. That same night I went out earlier from work, went to the other mill and asked to see the dyer in charge. When he was shown to me, I introduced myself and told him that, being in the same business, I was making a social call to get acquainted.

He was delighted and invited me to his place of business, showed me all around and had a nice chat until the whistle blew. Then we left together and proceeded to a place he knew, where we cemented our acquaintance, drinking to each other's health and future prosperity. He was a middle-aged man, had been with his firm over twenty years, having been transferred from a New England mill owned by the same company, and was getting ready to quit and go back to France, where he was born.

We had many acquaintances in common in the East, but he had not kept himself posted on the progress of the silk-dyeing industry. What he was trying then were just some experiments in weighting, as the management of his mill had heard about it and they wanted to see what could be done with it. They had hired a man to come up there from Paterson, N. J., to show them how to do the weighting properly. He was there three days and left without even getting his pay. He was a fraud, and had got scared and run away before finishing his first lot.

Somehow, my new-found friend told me, he put the

lot in shape and was trying to do the best he could, but did not think much of weighting silk. He was going to quit soon, anyway.

The next day I told my boss what I had learned. I said then that I knew we were as far ahead in our class of work as the best in the country.

When I returned my first lot loaded with sugar I got about 13 ounces. I did not like that, but I started on the glucose trial with a will to make a good showing at it. I took half a pound of gelatine and dissolved it by putting it to soak in cold water a couple of hours, and then boiling for a few minutes. Then I dissolved about 5 pounds of glucose in warm water and added to it the gelatine, stirring good, and let the whole cool off.

When it was cold, I poured water on this stock solution until it stood at 15 deg. Tw. I took my silk, dyed, and whizzed and worked it a handful at a time in the bowl, saturating it in this solution, adding new stock after every handful until all of it was saturated and wrung out. Then I whizzed it and put it in the drying room to dry. The result was all he desired and a little over, but I had to stringe the silk on the pin to make it soft and pliable. Next I started the loading with tin. I told him I could now go as far as he wanted, up to 32 ounces to the pound; but he laughed and told me to go just one pass. Except that it was on a small scale, I did the operating the same as I explained in another paper [AMERICAN DYESTUFF REPORTER, July 26, 1926]. After I dyed it, the return, we found, was about 15 ounces to the pound. All we had to do now was to choose which one to adopt. Of course, I had to improve the finish somewhat. The tin-weighted required a finish with an olive oil emulsified with soda ash. In the glucose solution I had to add some olive oil soap solution to overcome the harshness. We got what we could out of the stock of tin and phosphate of soda we had bought, then discarded it and kept on loading with the glucose and gelatine, using it at 10 deg. Tw. strength. He secured the contract and never had any complaints.

In due time the partner from New York, needing money, offered to sell his stock to the president at the suggestion of the manager, who knew that the president had no money to spare and could not buy it. Upon his refusal to buy it for cash, he turned it over to the manager, who bought it in his father's name and kept it a secret until the end of the year, when a meeting of the stockholders took place, and at that time he announced what he had done and elected his father vice-president of the concern.

The wrath of the president, when he realized what had taken place, can easily be imagined. He raved, declared himself cheated, and said he was not going to stand for any such thing. He declared that the stock was to be put in trust and the balance of control kept as before. The stock was offered to him, it being well known that he could not raise the money with which to buy it. He went to court and lost the case. He went to a higher court and lost again. He swore that he would wreck the company, but he never offered to sell his share in the concern.

He found a man in New England who had just lost his job as superintendent in a big mill. This man had a few thousand dollars saved up, and together they started a new silk mill in Montreal to compete with our mill; and so we had the novel situation of a president and sales manager of a mill becoming a partner in a new mill started for the sole purpose of putting out of business his own and older concern. Sounds like a fish story, but that was exactly what had occurred.

The manager of the new mill was well posted on the manufacture of silk. His brother was the dyer in the mill where he had been superintendent, and he knew something about dyeing. He took with him a young man who had been assisting his brother in the dyehouse there, and together they managed the dyeing in the new place. Naturally, it was started on a small scale. For about six months they were creeping along, cutting down prices to a ruinous degree. It was only a question of who was going to last longer in that struggle.

We cut down on the expenses of the office. Since my workroom was next to the office, I was elected office boy so that the manager could be free to spend all the time he could spare from his bookkeeping in the mill and the shipping room. I was attending the telephone also.

One day we discovered that the new mill was buying our silk through some of the president's friends, changing the label and the boxes and selling it with their own brand name on it. We soon stopped that practice.

When we were quite certain that the new mill could not last much longer, since it was headed straight for ruin, a relative of the president very conveniently laid down and died, leaving him an insurance of several thousand dollars. That saved him and he promptly made overtures to buy our mill. My boss was glad to sell out at his own figures and the president moved over and combined the two mills.

The first official act he did was to fire me. The manager offered to take me with him as partner in a new mill as soon as he found a location, but I refused —and was glad to come back to the United States.

The total production of coal tar made from lignite in Czecho-Slovakia during 1926 is estimated at 7,000 metric tons, and that of coal from bituminous coal at 85,000 tons. Ten plants are engaged in the manufacture of lignite coal tar, while bituminous tar is produced by twelve coke-oven plants and numerous gas works. The entire coal tar production is distilled by one firm. Consumption of coal tar products in Czecho-Slovakia in 1926 is estimated to have been 3,000 metric tons of lignite tar and 40,000 tons bituminous tar.

CHICAGO DYESTUFF MEN TAKE DAY OFF

The Spectrum Club of Chicago held its annual outing at Fox Lake, Ill., on Friday, June 10. The party began Thursday evening at the Mineola Hotel, chaperoned by Mr. and Mrs. Faith, (con)genial proprietors of the delightful summer resort. At 9 a. m. Friday all hands answered roll call for the day's labor, and divots flew fast until sundown.

Winners of the events were:

Class A—First low net, G. H. Powell; second low net, A. H. Mease.

Class B—First low net, C. B. Fieldhouse; second low net, L. R. Fox.

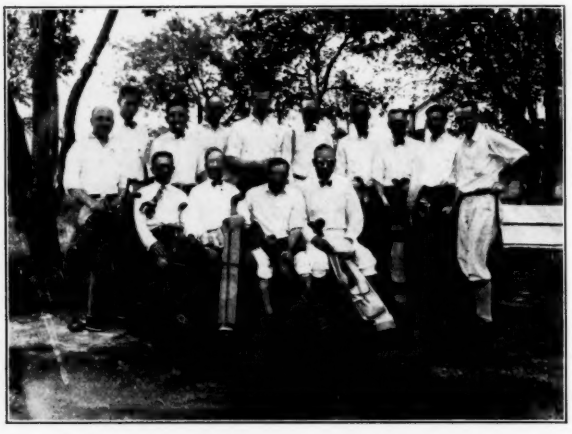
Blind Bogey—Class A, J. G. Stott, Jr.; Class B, A. L. Feit.

Barrel Hole—Class A, N. A. Ruston; Class B, L. R. Fox.

After an informal meeting and distribution of prizes, everybody hurried to the Riverside Inn at Wheeling, where the world's best chicken dinner was met and readily conquered. During dinner the members were entertained by Winner Powell (our songbird), the Hefti boys (father and son), buck-and-wing dancers, and Scotch (Dry) McKenna.

The committee in charge was A. T. Brainerd and J. W. Kopf. Officers for the year are F. N. Proudfoot, president, and P. O. May, secretary-treasurer.

Dr. E. W. Pierce, of New York, was a guest of the club and acted as official photographer for the day. One of his artistic triumphs is reproduced below.



Spectrum Club Outing

INDUSTRIAL PROCESS DEVELOPMENT

Industrial Processes Development, Ltd., has been incorporated in Toronto, Canada, with branches in Montreal, Ottawa, New York, and London, for the purpose of advising and assisting European firms and inventors in selling or establishing new processes in the United States and Canada, and to assist Americans similarly in Europe; to furnish reports on natural resources in Canada and their possibilities of development, and to carry out any technical investigations that may be necessary to find the most efficient and economical methods of utilization; and to assist in obtaining capital for the development of new industrial processes and patents. The directors of the company are F. W. Atack, R. T. Elworthy, J. W. Hughson, L. C. Jones, Dan McLachlin, F. R. Phelan and Howard Spence.

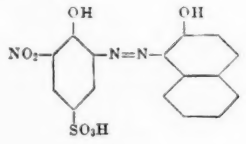
RECENT PATENTS

Dyestuffs, and Process of Making Same

(1,626,168; April 26, 1927)

Fritz Straub, Basel, Switzerland, assignor to the firm Society of Chemical Industry in Basle, Basel, Switzerland.

As new products the herein described acid wool dyestuffs containing chromium which have to be considered as complex chromium compounds of the azo dyestuffs corresponding with the formula:



which products form black powders dissolving in water with red-violet-black, in dilute caustic soda solution with violet-black coloration, dyeing wool from an acid bath reddish-black shades with excellent properties of fastness.

Dyestuffs Containing Chromium, and Process of Making Same

(1,626,169; April 26, 1927)

Fritz Straub, Basel, Switzerland, assignor to the firm Society of Chemical Industry in Basle, Basel, Switzerland.

A process for the production of new acid wool dyestuffs containing chromium, by treating azo dyestuffs containing chromable groups with chromium chromate.

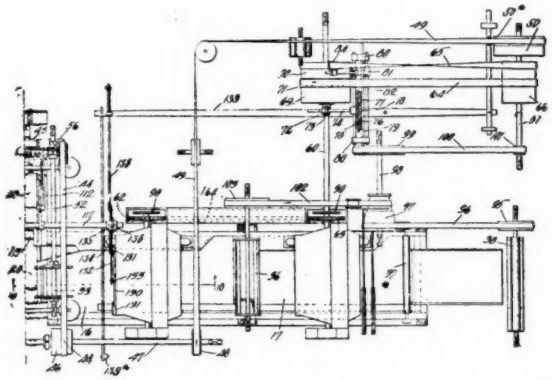
Apparatus for Cleaning Cloth

(1,628,690; May 3, 1927)

George Stone, North Andover, Mass., assignor to M. T. Stevens & Sons Company, North Andover, Mass., a corporation of Massachusetts.

In a web-cleaning apparatus, a rinsing tank having a partition subdividing the tank into two communicating compartments, a driven guide pulley arranged

to deliver a web to the first compartment, and a pair of driven feed rolls located one above the other above said partition, and arranged to withdraw the web from



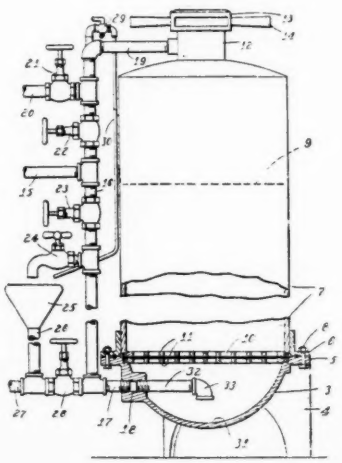
the first compartment and deliver it to the second compartment, the web passing in substantially parallel stretches from the first compartment to the feed rolls, and from the feed rolls to the second compartment, mechanism being provided for driving the feed rolls alternately forward and backward to reciprocate the web lengthwise.

Water Softener

(1,628,541; May 17, 1927)

Oscar W. Johnson, Rockford, Ill., assignor to Ward-Love Pump Corporation, Rockford, Ill., a corporation of Illinois.

The method of operating a base-exchange water softener which consists, first, in passing hard water through a zeolite material bed for softening; second, passing brine or other reagent with hard water through the bed of material in one direction for regenerating the same, and, third, passing hard water in the opposite direction through the bed to wash the same, the hard water being accompanied with a certain amount



of brine or reagent sufficient to regenerate whatever amount of material in the bed was exhausted in whole or part by the passage of the hard water with the brine through the material during regeneration.

Process of Coloring Materials

(1,627,939; May 10, 1927)

John P. Trickey, Evanston, Ill., assignor to the Quaker Oats Company, Chicago, Ill., a corporation of New Jersey.

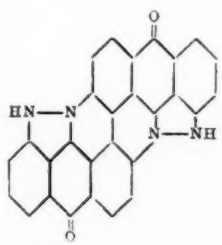
The process for coloring materials which comprises treating them with furfural, and then causing the furfural to impart color to said materials by an independent reaction in situ involving only the furfural and an acid agent.

Vat Dyestuffs of the Anthraquinone Series

(1,627,738; May 10, 1927)

Alfred Holl, Offenbach-on-the-Main, Germany, assignor to Grasselli Dyestuff Corporation, New York, N. Y., a corporation of Delaware.

As new products, vat dyestuffs of the anthraquinone series fast to alkali, which are reaction products of formaldehyde upon pyraxolanthron yellow compounds, to which the literature assigns the general formula:



in which the anthraquinone nucleus may be further substituted, which dyestuffs in a dry pulverized form are greenish yellow to orange yellow, soluble in sulphuric acid giving red-colored solutions and in boiling-hot nitrobenzol giving orange-yellow-colored solutions and which dye cotton from blue hydrosulphite vats reddish to greenish-yellow tints which are fast to alkali.

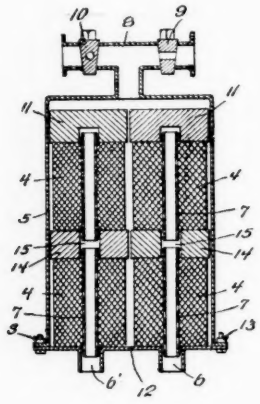
Means for Drying Textile Materials

(1,629,167; May 17, 1927)

Hermann Krantz, Aachen, Germany.

An apparatus for drying textile and the like materials, comprising a closable vessel for receiving the material to be dried, said vessel having at one end an opening communicating with the outer atmosphere and being provided at its other end with a controllable valve for connecting the vessel to a source of steam and with another controllable valve for connecting the vessel to a device for passing air through the vessel and the material contained therein, said material

having a perforated tubular member extending through the same and being in communication with the opening communicating the vessel with the outer

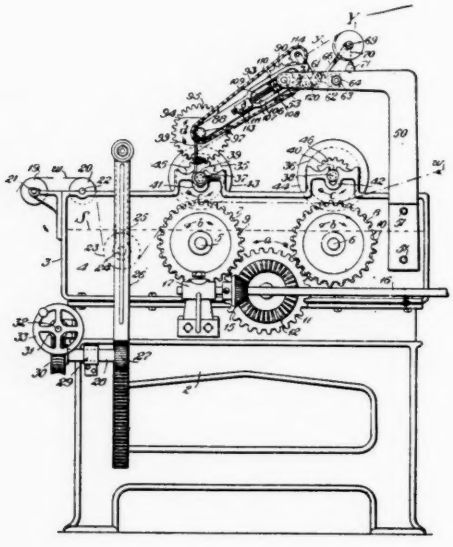


atmosphere, and a packing disk placed on the material which disk is provided with a recess for the reception of the end of said perforated tubular member.

Textile Processing or Finishing Machine

(1,628,261; May 10, 1927)

George J. McGann, Providence, R. I., assignor to Slasher Rolls Company, a corporation of Massachusetts.



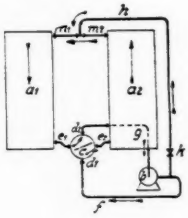
In a processing machine, the combination of cooperating rolls between which material passes, of which one is a press roll, and means whereby strand material may be applied to cover the face of said press roll by operating said machine.

Apparatus for Treating Vegetable, Animal or Artificial Fibers with Dyes or Other Liquids

(1,628,557; May 10, 1927)

Jacques Schlumpf, Oberwinterthur, Switzerland.

A dyeing machine of the type described, comprising a circulating pump, a circulating pipe system, two chambers adapted to receive the goods to be treated, said chambers being connected to the circuit of said



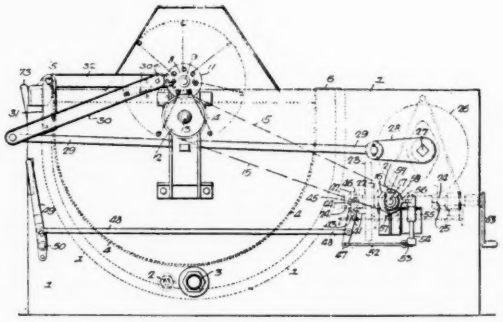
circulating pump, a reversing valve adapted to enable the direction of flow to be reversed at will in both chambers, and the system being provided with a single by-pass allowing the rate of flow of the dye in whichever chamber the flow is upward to be moderated at will.

Dyeing Machine

(1,627,347; May 17, 1927)

James H. Skitt, Philadelphia, Pa., assignor to Smith, Drum & Co., Philadelphia, Pa., a partnership consisting of Robert P. Smith and George E. Drum.

The combination with a vat of a cage adapted to occupy a position within the vat and movable with respect thereto, an agitator carried by the cage, a single power source adapted to move the cage and to operate



the agitator, separate clutches for respectively connecting the cage and the agitator with the power source, and means operatively connected with the cage for automatically interrupting the operation of the cage from the power source.

Weighting of Artificial Silk

(1,631,062; May 31, 1927)

George Rivat, Paterson, N. J., assignor to the Lyons Piece Dye Works.

Ordinary silk is weighted with tin by first treating it with a solution of tin chloride ($SnCl_4$), then washing the silk, treating with sodium phosphate, and, if desired, also with silicate of soda.

This process of tin-weighting, however, does not yield satisfactory results when applied, without modification, to artificial silk or artificial fibers made of acetate of cellulose. This material, which usually contains from 50 to 52 per cent of acetic acid bound as an ester of cellulose, is practically impermeable to water, and therefore absorbs but a very small proportion of the tin solution and of the sodium phosphate solution. For instance, with one type of acetate cellulose silk now on the market, the maximum gain in weight obtainable with the ordinary treatment is 2 per cent. The impermeability of this special artificial silk to aqueous solutions also reduces its capacity to take up usual dyestuffs; in fact, it is absolutely refractory to most dyestuffs.

The object of my present invention is to improve the weighting treatment to such an extent that artificial silk of the type set forth may take up a much higher percentage of the weighting agent (from thirty to more than fifty times the maximum obtainable hitherto).

Cellulose Acetate in State of Gel

In order to obtain these improved results, I bring the acetate of cellulose into a state of gel; that is to say, I modify its colloidal state so as to greatly increase its absorptive power. A gelling agent is a product which swells the cellulose acetate fiber and temporarily modifies its colloidal state by converting the cellulose acetate from a solid to a gel condition. When the fiber is in a gel state, it is particularly adapted to absorb other materials.

For the purposes of my present invention, cold aqueous solutions of formic acid or of acetic acid, in concentrations of from 15 to 20 per cent, have been found very efficient as gelling agents, enabling the acetate of cellulose fibers to absorb readily not only basic dyestuffs but the weighting agent (for example, tin chloride) as well. The gelling agent is brought in contact with the fibers either before they are treated with the tin chloride solution (or other weighting agent, such as a salt of any other heavy metal), or during the weighting treatment, or both before and during such treatment. When the gelling agent and the weighting agent are to act simultaneously, the addition, for example, of 75 c.c. of acetic acid to one liter of the customary tin chloride solution will be a suitable proportion.

After passing through the tin chloride solution (tin bath), the acetate of cellulose is washed carefully with water, thereby hydrolyzing the tin completely on the fiber. After this washing, no chlorine should be found on the fiber.

Into Formic Acid Solution

The acetate of cellulose is then gelled again by passing through a cold aqueous formic acid solution of a strength of from 15 to 20 per cent, then washed with water, and subsequently passed through a warm sodium phosphate bath (at a temperature of from 40 to 45 deg. Cent.), this sodium phosphate treatment being performed in the same manner as is customary in the case of weighting natural silk. This sodium phosphate bath is used for the purpose of fixing the tin. After the fixing (phosphating) treatment a further treatment with silicate of soda may be employed in some cases, if desired.

The treatment consisting of these steps of gelling, tin-weighting, washing and fixing (phosphating), and, if desired, treating with silicate of soda, may be repeated once or oftener to increase the amount of weighting agent absorbed. Very high weighting percentages may thus be obtained; for instance, 75 per cent, 100 per cent, or even more.

Acetate of cellulose products when weighted as described above lose none of their desirable qualities. The artificial silk thus created remains soft and lustrous, and keeps all its original selective affinities for dyestuffs. In fact, these affinities are enhanced, and in particular the affinity for certain dyestuffs, such as the SRA (sulpho ricinoleic acid dyestuffs), is increased very materially by the weighting treatment described.

Condition Does Not Matter

I desire it to be understood that my invention is applicable to acetate of cellulose fibers or products irrespective of their condition; that is, whether they be in the nature of threads, skeins, fabrics, etc. Furthermore, these fibers may be treated either alone or in conjunction with others; as, for instance, in the case of mixed woven fabrics which consist only partly of acetate of cellulose.

Various modifications may be made without departing from the nature of my invention as set forth in the appended claims.

What is claimed is:

1. The process which comprises treating cellulose acetate silk with a gelling agent and with a weighting agent.

2. The process which comprises treating cellulose acetate silk with a gelling agent and with a weighting agent comprising a suitable salt of a heavy metal.

3. The process which comprises treating cellulose

acetate silk with a gelling agent and with a tin chloride weighting solution.

4. The process which comprises treating cellulose acetate silk with a gelling agent and with a tin chloride weighting solution, then washing the product and treating it with a suitable fixing agent.

5. The process which comprises treating cellulose acetate silk with a gelling agent and with a tin chloride weighting solution, then washing the product thus treated, then again treating with a gelling agent, and thereupon treating the product with a suitable fixing agent.

6. The process which comprises treating cellulose acetate silk with a gelling agent and with a weighting agent, washing the product thus treated, again treating with a gelling agent, and then treating the product with a fixing agent.

7. The process which comprises treating cellulose acetate silk with a gelling agent and with a solution of a weighting agent comprising a suitable salt of a heavy metal, then washing the product thus treated, and then treating it with a fixing agent.

8. The process which comprises treating cellulose acetate silk with a gelling agent and with a solution of a weighting agent comprising a suitable salt of a heavy metal, then washing the product thus treated, then again treating with a gelling agent, and thereupon treating the product with a fixing agent.

9. In the process of weighting cellulose acetate silk, the step which comprises treating the silk with a gelling agent.

10. In the process of weighting cellulose acetate silk, the step which comprises treating the silk with a solution of a water-soluble aliphatic acid having a concentration of 15 to 20 per cent.

11. The process of weighting cellulose acetate silk which comprises treating the silk with a solution of a water-soluble aliphatic acid, and then subjecting the so-treated silk to the usual weighting agents.

12. The process of weighting artificial silk which comprises treating cellulose acetate with a solution of a water-soluble aliphatic acid having a concentration of not more than 20 per cent, and then subjecting the so-treated silk to a solution of tin chloride.

13. The process of weighting artificial silk which consists in treating cellulose acetate with a solution of a water-soluble aliphatic acid having a concentration of 15.50, 20 per cent, subjecting the so-treated silk to the action of a solution of tin chloride, washing the silk with water and subsequently treating the silk with a warm solution of sodium phosphate.

Preparation and Dyeing of Leather

(1,628,160; May 10, 1927)

Morris Charles Lamb, Bermondsley, London, England.

In the dyeing of leather, treating the leather with an emulsion of hydrogenated naphthalene and with a dyeing agent.

HOSIERY COLORS FOR FALL

The hosiery colors issued for fall, 1927, by the Textile Color Card Association in co-operation with the National Association of Hosiery and Underwear Manufacturers comprise delicate shades for evening and darker tones for daytime wear.

The new evening tints are Opera Pink—a rose which harmonizes with Debutante Pink on the fall, 1927, card; Opal Mauve—a pale violet; and Vanity—a nude shade. Other colors featured include Mirage, a grayish beige; Yosemite, a golden luster appropriate for autumn, and Bronze Nude, a medium brown; Seasan, a light grayish tan; Manon, a medium brownish gray; Merida, a soft cafe-au-lait color; Beechnut, a shade darker, and Rifle, a dull slate gray.

Some colors repeated from former cards because of their popularity are Harvest, Moonlight, French Nude, Grain, Dove Gray, Evenglow, Blue Fox, Aloma and Beige.

Also incorporated in the hosiery card are the shoe colors, giving the additional service of a combined shoe, hosiery and leather card, and a composite picture of the colors featured by these related industries. The six fall shoe colors chosen by the allied shoe and leather committee appointed by the Tanners' Council, National Boot and Shoe Manufacturers' Association and the National Shoe Retailers' Association, in co-operation with the Textile Color Card Association, are Brierwood, a mahogany; Andorra, a deep-toned brown, and Whippet, a neutral shade bordering on fawn. The well-known Stroller Tan, a rust shade; Sauterne, a light gold-tinted tan, and Plaza Gray, a medium tone, have been retained.

ARABS USE HENNA FOR DYEING

The well-known "henna" used throughout the East for decorative staining of the hands, feet and nails of women, and sometimes men, and of the manes and tails of horses, is sometimes used for commercial decoration of sacrificial sheep, goats and other animals, as well as for the purpose of marking herds for identification purposes. The women of the Eastern races are especially given to the use of henna dye, particularly in the preparation of their toilet for weddings and other public ceremonies, according to the Department of Commerce, Chemical Division.

Henna in its commercial form appears in the market as a fine powder, usually having a greenish hue, although the dye when applied turns to various shades of orange and red. It is prepared by powdering the dried leaves of the typically Arabian plant called "Lawsonia Alba" growing in greatest profusion in the coastal region of Jisan, in Assir, on the middle Red Sea littoral of the Arabian Peninsula. The common name "henna" is pure Arabic, applied to the dye from time immemorial, and as far as can be ascertained has no basic meaning. It is simply the native name for the plant. The plant itself is a small, thorny desert shrub which grows in profusion even where water seems to be wanting.

DU PONT DEVELOPS TWO MORE COLORS

An entirely new diazo color and an olive drab sulphur dye have been perfected in the dyestuff laboratories of E. I. du Pont de Nemours & Co. and placed on the market, the former under the title Pontamine Diazo Orange G and the latter as Sulfogene Olive Drab Y.

The new Pontamine color, for which a patent has been applied, yields orange tones described as of great brilliance and of the highest fastness. It is developed with beta-naphthol and its solubility is said to be very good. It is also said to dye very evenly and exhaust clearly, and can therefore be used on all types of machines in which diazo colors are usually applied. It is suitable for both self-shades and in combinations, being particularly adapted for the latter on account of its easy working properties. It can be dyed on silk and rayon, but Celanese is left unstained.

On union material Pontamine Diazo Orange G dyes silk, wool and cotton to approximately the same depth, the animal fibers dyeing a little yellower. It is claimed further to discharge to a clear white with Sulfoxite G on both cotton and silk.

Sulfogene Olive Drab Y is also described as having excellent dyeing properties, a solubility and good penetration. It can be used for all types of machine dyeing. The shade is such, according to the description, that it can substitute the usual combinations of sulphur colors employed for olive drab and similar shades.

Used without aftertreatments, it is further claimed, Sulfogene Olive Drab Y gives a bright greenish olive drab with fastness only slightly inferior to that of the aftertreated dyeings, except where fastness to mercerizing is required.

CALCO TAKES OVER WILLIAMSBURG CHEMICAL COMPANY

The business and good-will of the Williamsburg Chemical Company, of Brooklyn, have been purchased by the Calco Chemical Company, of Bound Brook, N. J., according to announcements issued by both interests.

The Williamsburg Chemical Company manufactured a group of basic colors, including Malachite Green, Brilliant Green, Methylene Blue and Safranine. The Calco Company have been large manufacturers of basic colors and intermediates, and because of its facilities, it is pointed out, is particularly fitted to carry on the work and business of the Williamsburg Company.

The Payson Yarn Company, distributors of natural, bleached and colored yarns in cones, tubes and cops, is now located at larger quarters at 663 Broadway, New York.

SOUTHERN TEXTILE CHEMISTS TO MEET JULY 16

A joint meeting of the Piedmont and South Central Sections of the American Association of Textile Chemists and Colorists has been arranged and will be held at the George Vanderbilt Hotel, in Asheville, N. C., on Saturday evening, July 16.

A baseball game will be played in the afternoon between the married and single men of these two sections. A full program of technical papers has been arranged for the evening meeting, which it is hoped will be made even more interesting by discussions of the subjects presented.

T. C. King, superintendent of dyeing, bleaching and finishing, of the Cramerton Mills, Inc., Cramerton, N. C., will discuss "The Dyeing and Finishing of Celanese." Carl C. Poindexter, chemist of the Chatham Manufacturing Company, Elkin, N. C., will discuss "The Dyeing and Finishing of Woolen Blankets."

John L. Crist, general manager of the Beaver Chemical Corporation, Damascus, Va., will discuss "The Manufacture of Sulphur Colors." A. R. Thompson, Jr., Southern manager of Rohm & Hass Company, Inc., Charlotte, N. C., will discuss "The Uses of Hydrosulphite in the Textile Industries."

RAYON TRUST IN ITALY

A pooling of trade secrets and patents, as well as technical research, has resulted from the recent agreements made by the Snia Viscosa Artificial Silk Company, of Turin, Italy, with two of its strongest rivals, Courtalds Ltd., of London, and the Vereinigte Glanzstoff-Fabriken A. G., of Elberfeld, Germany. This advice comes from Consul H. T. Mooers at Turin, who reports further that the new arrangement will obviously bring about a standardized product and lower prices, and give to this group a distinct advantage over foreign competitors. It is reported from reliable sources that the Snia has increased its production since the first of this year by 33 per cent as compared with the same period during 1926.

ON LIQUID CAUSTIC SODA

The use, handling and storage of liquid caustic soda is treated in an interesting manner and in considerable detail in a bulletin recently issued by the Mathieson Alkali Works, Inc. The purpose of the bulletin is to explain the facts about the liquid form of the chemical to those interested in changing from the solid soda, and to place in the hands of those now using the liquid caustic some useful data on approved methods for its transfer, handling and storage, together with some notes on the dilution, testing and properties of caustic liquors. The bulletin is illustrated with photographs of tank-car equipment and diagrams showing unloading methods. It may be obtained by interested consumers from the Mathieson Alkali Works.

SALT USED IN WATER SOFTENERS STUDIED

Determination of the proper grade of salt for use in zeolite water softeners has been the subject of studies undertaken by the research division of the International Salt Company, manufacturers of all types of sodium chloride.

The salt brine necessary for the regeneration of the zeolite in water softening can be produced with any grade of common salt, and users of water softeners have in the past proceeded on this principle; but it is pointed out in the report of the International Salt Company's researches that the size and capacity of the softener influences the choice of salt where economy is sought. As the result of its study on this subject, the company announces a policy of recommending only the proper grade of salt to meet requirements of various types of softeners.

FRENCH WORKING TOWARD LARGER CHEMICAL TRUST

Recent movement observed in the French chemical and dyestuff industry have given color to the belief that further combination of its units at home is being attempted while overtures for an agreement with the German industry are also being made. In fact, it is fully expected that a definite alliance with the German Cartel will be effected during the early part of this summer, according to a very interesting survey of the French chemical industry received by the Department of Commerce from Trade Commissioner Daniel J. Regan, stationed at Paris.

Parallel with these negotiations for an international dyestuffs entente, efforts are still being made to combine several of the leading French chemical companies. Although it has been officially denied that a combination has just been effected between Poulenc Freres and the Usines du Rhone, it is known that these two companies, specializing in pharmaceutical products, are still working on a plan for the combination of their resources. A similar effort is directed toward a working combination between St. Gobain, Kuhlmann and Pechiney (Compagnie d'Alais, Froges et Camargue), three of the largest French chemical companies.

These efforts of private companies to effect combinations to avoid wasteful competition and to co-ordinate their direction and use of equipment have been regarded as absolutely necessary by leaders of the industry. It would appear that the concentration which has been going on since the war within the various branches of the industry is now to be followed by a fusion among the principal groups. According to the managing director of the Kuhlmann Company, "the chemical industry in France, where the spirit of individualism is so strongly imputed, since the war has felt, however confusedly, that it cannot escape the universal tendency toward concentration already so developed in Germany and now in England."

As a step toward the unification of the French chemical industry, a directive organization has been formed, known as the Comite des Industries Chimiques, to be the mouthpiece for the chemical industry as the Comite des Forges has long been for the French steel companies. The avowed purpose of this national committee, made up of representatives of the leading French chemical companies, is to maintain a permanent contact among the various branches of the industry. Through this central organization it is hoped to co-ordinate, and, where desirable, to work for the unification of the various branches of the industry. These will be able to exert their influence in regard to such matters as changes in tariffs, commercial treaty negotiations and legislation relating to the industry, as well as to work for the co-ordination and better utilization of chemical resources, equipment and power.

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i. e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

DYER'S ASSISTANT

German dyer, experienced on cotton, mercerized cotton and rayon, both skeins and piece goods, seeks position as assistant to dyer. Address Classified Box 406, American Dyestuff Reporter.

COLOR CHEMIST

Experienced in standardizing and application of all classes of colors on textiles, matching and mixing, would like position in mill or laboratory. Address Box 408, American Dyestuff Reporter.

DYE PLANT

Well-equipped dye plant for bleaching and dyeing; about 75 by 100; in New Durham, N. J.; on reasonable terms. Good opportunity for small dyer to start in business. For information apply to The Inflexible Company, 313 Eleventh Street, West New York, N. J

WANTED

Salesman to represent old-established firm throughout New England and Canada, to push sales of their products consisting of Dyeing Machinery for hosiery and yarn, as well as Mercerizing Machinery. Must be a technically trained dyer and at same time be well versed mechanically. Full details in first letter. Address Box 409, American Dyestuff Reporter